ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

ONE-POT SYNTHESIS OF GRAFT POLYMERS VIA DIELS-ALDER REACTIONS

M.Sc. THESIS

İpek YİĞİT

Department of Chemistry

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

DIELS-ALDER REAKSİYONLARI İLE TEK ADIMDA AŞI POLİMERLERİ SENTEZİ

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İpek YİĞİT, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID **509101063**, successfully defended the **thesis** entitled "**One-Pot Synthesis of Graft Polymers Via Diels-Alder Reactions**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family,

FOREWORD

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TABLE OF CONTENTS

Page

ABBREVIATIONS

^{1}H NMR : Hydrogen Nuclear Magnetic Resonance Spectroscopy
ATNRC : Atom Transfer Nitroxide Radical Coupling
ATRP : Atom Transfer Radical Polymerization
$CDCl_3$: Deuterated chloroform
CH_2Cl_2 : Dichloromethane
C/LRP : Controlled/Living Radical Polymerization
CuAAC : Copper catalyzed azide-alkyne cycloaddition
DA : Diels-Alder
DMF : *N*,*N*-dimehthylformamide
EtOAc : Ethyl acetate
GPC : Gel Permeation Chromatography
PONB : Poly(oxanorbornene)
PDI : Polydispersity Index
PEG : Poly(ethylene glycol)
PMDETA : *N, N, N',N'', N''*-Pentamethyldiethylenetriamine
PMMA : Poly(methylmetacrylate)
P*t*BA : Poly(*tert*-butyl acrylate)
RAFT : Reversible Addition Fragmentation Chain Transfer
NMP : Nitroxide Mediated Polymerization
ROMP : Ring Opening Metathesis Polymerization
ROP : Ring-opening polymerization
TD-GPC : Triple Detector-Gel Permeation Chromatography
Et_3N : Triethylamine
TEMPO : 2,2,6,6-Tetramethylpiperidine-*N*-oxyl
THF :Tetrahydrofuran
ε-CL :ε-caprolactone
PCL :Poly(ε-caprolactone)

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SYMBOLS

A	**:** Absorbance
k_{act}	**:** Activation
°C	**:** Celcius
Mp	**:** Melting point
M	**:** Molarity
nm	**:** Nanometer
ppm	**:** Parts per million
$R^{\cdot}$	**:** Radical
R_p	**:** Rate of polymerization
d*n*/dc	**:** Refractive index increment
M_w/M_n	**:** Polydispersity index
M_n	**:** The number average molecular weight
M_w	**:** The weight average molecular weight
λ	**:** Wavelength

ONE-POT SYNTHESIS OF GRAFT POLYMERS VIA DIELS-ALDER REACTIONS

SUMMARY

The Ring Opening Metathesis Polymerization (ROMP) of cyclic olefins by using metal alkylidene initiators has led to a number of well defined architectures including block, graft, star, and cyclic polymers which has controlled moleculer weight and controlled end group.

Graft polymers have a considerable interest because of having nonlinear architecture with different composition and topology. Because of their branched structure they generally have also lower melt viscosities, which is advantageous for processing. Also, graft polymers have a better physical and chemical properties than their linear polymers. Graft copolymers can be obtained with three general methods: (i) grafting-onto, in which side chains are preformed, and then attached to the backbone; (ii) grafting-from, in which the monomer is grafted from the backbone; and (iii) grafting-through, in which the macromonomers are copolymerized.

In recent years, the use of controlled/living radical polymerization techniques in the synthesis of complex macromolecules (star and graft polymers) has quickly increased because of the variety of applicable monomers and greater tolerance to experimental conditions in comparison with living ionic polymerization routes. Nitroxide mediated radical polymerization (NMP) based on the use of stable nitroxide free radicals and Metal/ligand catalyst-mediated living radical polymerization, which is often called atom transfer radical polymerization (ATRP), are versatile methods among living radical polymerizations.

In first part of this study; anthracene-functionalized oxanorbornene monomer were polymerized via ring opening metathesis polymerization (ROMP) using the first generation Grubbs' catalyst in dichloromethane at room temperature and then maleimide end-functionalized polymers, PEG-MI, PMMA-MI, and P*t*BA-MI were synthesized via ATRP and Poly(ε-caprolactone) PCL was synthesized via Ring Opening Polymerization (ROP) and maleimide functionalized via esterification reaction.

In the second part of this study, PMMA-MI, PEG-MI and P*t*BA-MI or PCL-MI are grafted to these ROMP copolymers for the first time in a one-pot fashion via Diels-Alder reactions in toluene/dioxane mixture at 110 ^{o}C to create corresponding graft copolymers poly(oxanorbornene)-*g*-PEG-P*t*BA-PMMA or poly(oxanorbornene)-*g*-PEG-P*t*BA-PMMA.

Diels-Alder reaction efficiency for graft copolymerization was monitored by UV-Vis spectroscopy. The d*n*/d*c* values of graft copolymers were experimentally obtained using a triple detection GPC (TD-GPC) and subsequently introduced to the software so as to give molecular weights, intrinsic viscosity ([η]) and hydrodynamic radius (Rh) values.

DIELS-ALDER REAKSİYONLARI İLE TEK ADIMDA AŞI POLİMERLERİ SENTEZİ

ÖZET

Kontrollü kompozisyon ve yapılarda iyi tanımlanmış makromoleküllerin sentezi polimer biliminde yeni bir alan açan iyonik polimerizasyon yöntemlerinin gelişimine kadar kimyagerler için sorun olmuştu. Ancak, iyonik polimerizasyon araştırmalarının gelişimi zorlu işlem koşulları; yüksek saflık ve çeşitli fonksiyonel monomerlerle uyumsuzluk söz konusu olduğundan bazı ciddi engeller ile karşılaşmaktadır. Serbest radikal polimerizasyonu safsızlıklara daha toleranslıdır ve çok çeşitli vinil monomerlerinin polimerleştirilmesi yeteneğine sahiptir fakat en büyük dezavantajı iyonik polimerizasyondaki gibi polimer yapı ve fonksiyonalite kontrolünün aynı derecede mümkün olmamasıdır. Bu nedenle, kaydadeğer çabalar serbest radikal polimerizasyonunu kontrollü bir şekilde gerçekleştirmek için harcanmıştır. Neyse ki, serbest radikal polimerizasyonunundaki devrim herhangi bir zorlu deneysel koşul gereksinimleri olmayan, iyi tanımlanmış makromoleküllerin inşasına erişim kolaylığı sağlayan kontrollü/"yaşayan" radikal polimerizasyon (C/LRP) yöntemlerinin gelişimlerine yol açmıştır.

Son yıllarda, kompleks makromoleküllerin sentezinde kontrollü/yaşayan polimerizasyon tekniklerinin kullanılması, yaşayan iyonik polimerizasyon yöntemiyle mukayese edildiğinde deneysel koşullara daha fazla toleranslı olması ve çok çeşitli monomerlere uygulanabilir olması nedeniyle hızlı bir şekilde arttı. Kararlı nitroksit serbest radikallerin kullanımına dayanan Nitroksit Ortamlı Radikal Polimerizasyonu ve genellikle Atom Transfer Radical Polimerizasyonu (ATRP) olarak bilinen Metal/ligand kataliz ortamlı radikal polimerizasyonu yaşayan radikal polimerizasyon yöntemleri arasında çok yönlü metotlardır.

Son yıllarda, Sharpless ve arkadaşları azidler ve alkin/nitriller arasındaki Huisgen 1,3-dipolar siklokatılmalarda ([3 + 2] sistemi) Cu(I)'i baz ile birleştirip kataliz olarak kullandılar ve bu reaksiyonu click reaksiyonu olarak adlandırdılar. Daha sonra click kimyası blok kopolimerlerden karmaşık makromoleküler yapılara kadar değişen birçok polimerik malzemenin sentezinde başarılı bir şekilde uygulandı. Click reaksiyonları, yan reaksiyonlara neden olmadan ve ilave saflaştırma işlemlerine gerek duyulmadan kantitatif verimle C–C (veya C–N) bağ oluşumuna izin vermektedir. Diels-Alder reaksiyonları ise konjuge bir dien ile dienofil bileşiğinin siklo katılması olarak bilinir ve makromoleküllerin sentezinde önemli bir yere sahiptir.

ATRP'nin temeli, radikal oluşumu ve polimerizasyonun oluşan radikal üzerinden yürümesidir. Radikal polimerizasyonu birkaç monomerden yüzlerce monomere kadar polimerleşmeyi gerçekleştirebildiği gibi, su ortamında emülsiyon ya da süspansiyon polimerizasyonunu da mümkün kılar. ATRP'de kullanılan geçiş metallerinin halojenli bileşikleri, redoks reaksiyonu ile indirgenip-yükseltgenerek,

tersinir bir mekanizmayı meydana getirir. İşte bu tersinir mekanizma ile polimer zincirleri neredeyse aynı anda meydana gelerek, düşük polidispersiteli polimerlerin eldesini sağlar. Diğer bir sentez türü ROP ise, makromoleküler malzemelerin sentezinde geniş ölçüde uygulanarak, halkalı monomerlerin açılmasıyla lineer polimerlere dönüşmesini sağlayan eşsiz bir polimerleşme türüdür.

Metal alkilidin kullanarak siklik olefinlerin Halka Açılma Metatez Polimerizasyonu (ROMP) ile blok, aşı, yıldız ve siklik polimerler gibi uç grup kontrolü, moleküler ağırlık kontrolü gibi özelliklere sahip birçok iyi tanımlı yapılar elde edilebilir. Halka açılma metatez polimerizasyonu siklik olefinlerden doğrusal makromoleküler yapıdaki bileşiklerin kısa sürede elde edilme imkanı veren polimerizasyon türüdür. Bu polimerizasyonda olefin metatez için gerekli iki olefinden biri monomer diğeri ise katalizördür. Monomer olarak bir siklik olefin ve katalizör olarak metal alkilidin kullanılır.

En genel ROMP polimerleri norbornen tipi monomerlerden türetilir. Norbornen yapısı fonksiyonel grupların polimerlerdeki çeşitliliğini belirtmek için kullanılır. Yüksek camsı geçiş sıcaklığı ve iyi ısıl kararlılığı gibi önemli özellikleri polinorbornen iskeleti ile ilişkilidir. Tek dezavantajı hava ile temasında çabuk okside olmasıdır bu da hidrojenerasyonla engellenebilir.

Ayrıca serbest radikal polimerizasyonu gibi diğer ticari polimerizasyon teknikleri karşılaştırıldığında ROMP-norbornen sistemi çok daha üstündür. Radikal polimerizasyonunun en büyük problemlerinden biri zincir transferi ve sonlandırma işleminden dolayı molekül ağırlığı kontrolüdür. Kontrollü/yaşayan serbest radikal polimerizasyonu nitroksit ortamlı radikal polimerizasyonu ve atom transfer radikal polimerizasyonu ile sağlanır. Fakat bu yaşayan polimerizasyonların genellikle tamamlanması için uzun reaksiyon süresi gerekir. Molekül ağırlığı kontrolü yaşayan iyonik polimerizasyonlar da başarılı olunabilir.

Aşı polimerler sahip olduğu lineer olmayan yapısı, farklı bileşimi ve topolojisi nedeniyle önemli bir ilgiye sahiptir. Dallı yapılarından dolayı genellikle düşük vizkozite değerlerine sahiptir ve bu durumda polimerin işlenme koşullarını kolaylaştırır. Ayrıca, aşı polimerler lineer polimerlere kıyasla daha iyi fiziksel ve kimyasal özelliklere sahiptir.

Bu çalışmada temel olarak Halka-Açılma Metatez Polimerizasyonu (ROMP) ve Diels-Alder reaksiyonları gerçekleştirilerek tek adımda değişik kompozisyonlarda ve yapılarda aşı kopolimerleri sentezlenmesi amaçlanmıştır.

Bu tezde, ilk aşamada antrasen fonksiyonlu okzanorbornen monomeri oda sıcaklığında diklorometan içerisinde birinci jenerasyon Grubbs katalizörü kullanılarak Halka Açılma Metatez Polimerizasyonu ile polimerleştirilip poli(okzanorbornen) (PONB) kopolimeri elde edilmiştir. Maleimid uç fonksiyonlu polimerler PMMA-MI ve P*t*BA-MI ise Atomik Transfer Radikal Polimerizasyonu (ATRP) yöntemi ile sentezlenmiştir. Poli(etilenglikol) (PEG) ise esterleşme reaksiyonu ile maleimid fonksiyonlandırılmıştır. Poli(ε-kaprolakton) (PCL) ise Halka Açılma Polimerizasyonu (ROP) yöntemi ile sentezlenmiş ve esterleşme reaksiyonu ile maleimid fonksiyonlandırılmıştır.

İkinci aşamada poli(okzanorbornen) (PONB) kopolimerinde bulunan yan fonksiyonlara tek aşamada 3 farklı maleimid uç fonksiyonlu polimer takılarak aşı kopolimerler sentezlenmiştir. Bu amaçla, PMMA, PEG ve P*t*BA veya PMMA, PEG, PCL'den oluşan 3 farklı polimer sistemi PONB kopolimerine tek aşamada 110 ^{o}C'de

toluen/dioksan karışımı içerisinde aşılanmıştır ve sırasıyla poly(okzanorbornen)-*g*-PEG-P*t*BA-PMMA veya poli(okzanorbornen)-*g*-PEG-PCL-PMMA aşı polimerleri sentezlenmiştir.

Bu çalışma sayesinde ROMP ve Diels-Alder reaksiyonlarının bir arada kullanılmasıyla değişik kompozisyonlarda ve yapılarda aşı polimerler tek aşamada başarıyla sentezlenmiştir.

Aşı kopolimerizasyonun Diels-Alder reaksiyonu etkinliği UV-Vis spektroskopisi ile gözlemlendi. Aşı kopolimerlerinin d*n*/d*c* değerleri üçlü dedektör GPC (TD-GPC) kullanılarak elde edildi ve bu değerler cihaza tanıtılarak molekül ağırlıkları, intrinsik viskozite ([η]) and hidrodinamik yarıçapı (Rh) değerleri elde edildi.

1. INTRODUCTION

A combination of living polymerization methods and their compatible partner click reactions allows increasingly the synthesis of the complex macromolecular structures, such as star, cyclic, hyperbranched polymers, dendrimers, and graft copolymers, with well-defined molecular weight, composition, topology and functional groups [1-13]. It is well known that complex architectures display different properties both in bulk and solution, i.e. morphology and assembly in solution and in bulk, and the solution and the melt viscosity, while compared to their linear counterparts.

Graft copolymers can be obtained with three general methods: (i) grafting-onto, in which side chains are preformed, and then attached to the main polymer backbone; (ii) grafting-from, in which the monomer is grafted from the main backbone; and (iii) grafting-through, in which the macromonomers are copolymerized in order to give the resultant graft copolymer [14, 15].

Among living polymerization methods, ring opening metathesis polymerization (ROMP) is a versatile and an efficient synthetic strategy for the polymerization of cyclic olefins (such as norbornene norbornadiene, and dicyclopentadiene etc.) by using metal alkylidene initiators (e.g. molybdenum and ruthenium complex catalysis) [16-34]. Although there have been many published studies on the synthesis of graft copolymers by using a combination of ROMP and other living polymerization techniques ; such as ROMP-ROMP, ROMP-atom transfer radical polymerization (ATRP), ROMP-reversible addition fragmentation chain transfer polymerization (RAFT), ROMP-living anionic polymerization, and ROMP-ring opening polymerization (ROP) combinations , relatively few publications have emerged in the literature based on combining ROMP and “click” reactions [35-52]. Grubbs first time employed a ROMP-“click” combination for the synthesis of graft copolymers using grafting-through method [53].

Recently, our group has reported the synthesis of well-defined graft and heterograft

copolymers via combination of living radical polymerization techniques with "click" reactions: Diels-Alder and copper catalyzed azide-alkyne cycloaddition reaction [54, 55]. More recently, our group has demonstrated the synthesis of various types of star polymers by a ROMP-azide alkyne "click" reaction combination [56, 57].

In this thesis; we first time applied ROMP-Diels Alder combination to graft maleimide functionalized polymers to a polymer backbone in a one-pot fashion via grafting-onto method.

For this purpose, anthracene-functionalized oxanorbornene monomer were polymerized via ROMP using the first generation Grubbs' catalyst and polymer backbone was obtained. The functionalized polymers were analyzed by ^{1}H-NMR and GPC measurement.

As a second step, same equivalent of maleimide end- functionalized polymers, PMMA-MI,P*t*BA-MI PEG-MI or PMMA-MI, PCL-MI, PEG-MI are grafted to ROMP copolymer in a one-pot fashion via Diels-Alder reactions to obtain graft copolymers poly(oxanorbornene)-*g*-PEG-P*t*BA-PMMA or poly(oxanorbornene)-*g*-PEG-PCL-PMMA.

Representative structures are shown in Figure 1.1.

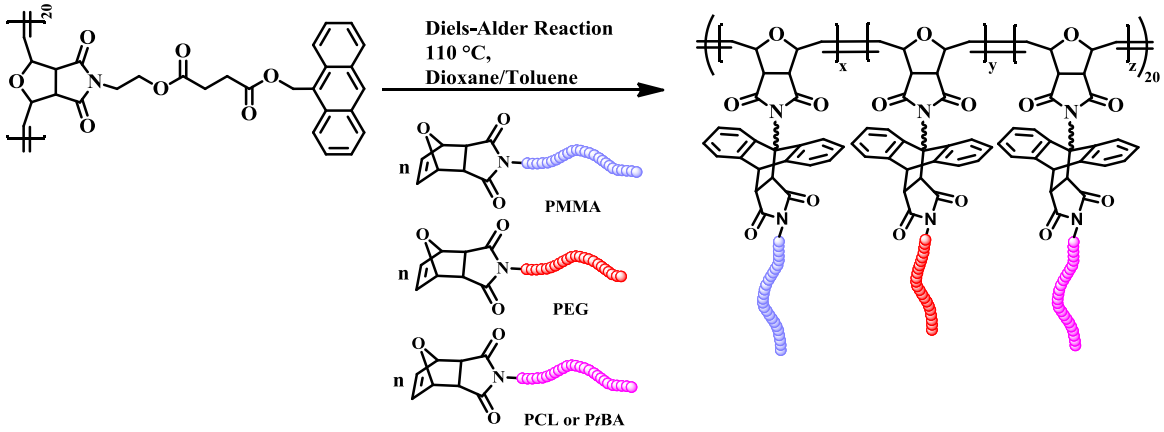


Figure 1.1: General scheme for the preparation of graft copolymers via ROMP and Diels–Alder reaction.

2. THEORETICAL PART

2.1 Controlled/ ‘‘Living” Polymerizations

A living polymerization is defined as a chain polymerization without chain transfer and chain termination as indicated by Szwarc. Well-defined polymers, can only be synthesized by living ionic polymerizations or controlled/ “living” radical polymerization (C/LRP) methods [58]. Until recently, ionic polymerizations (anionic or cationic) were the only living techniques that efficiently controlled the structure and architecture of vinyl polymers. These polymerization techniques ensure low polydispersity materials, controlled molecular weight and defined chain ends but they are not useful for the polymerization and copolymerization of a wide range of functionalized vinylic monomers [59]. Furthermore, these techniques require stringent reaction conditions and pure reagents. To overcome all these limitations polymer chemists developed new concepts. These new concepts are often called controlled radical polymerization, living radical polymerization, control/“living” radical polymerization [60, 61].

Living polymerization provides end-group control and enables the synthesis of block copolymers by sequential monomer addition. However, it does not necessarily provide polymers with molecular weight (MW) control and narrow molecular weight distribution (MWD). To obtain well defined polymers the initiator should be consumed at early stages of polymerization and that the exchange between species of various reactivities should be at least as fast as propagation [62-64].

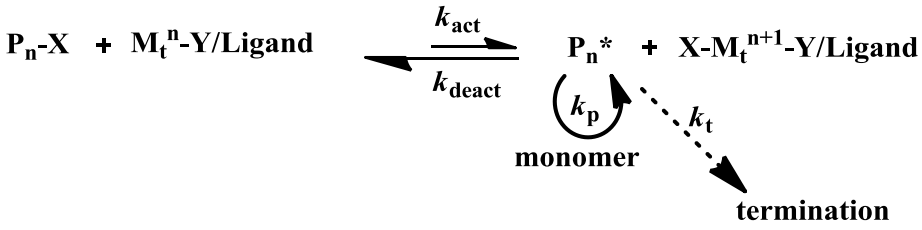
2.2 Controlled/ ‘‘Living” Radical Polymerizations

Living free radical polymerizations have attained a tremendous following in polymer chemistry. A great deal of effort has been made to develop and understand different living free radical polymerization (LFRP) methods. Georges and co-workers first introduced true nitroxide mediated polymerization (NMP) in 1993, Matyjaszewski

and Sawamoto developed metal catalzed (Cu, Ru) living radical polymerization also called atom transfer radical polymerization (ATRP) in 1995, and Moad, Rizzardo and Thang reported reversible addition-fragmentation chain transfer polymerization (RAFT) in 1998 [68-71].

2.2.1 Atom transfer radical polymerization (ATRP)

Atom transfer radical polymerization (ATRP) is a living radical polymerization process, which is consisting of the monomer, initiator, and catalyst composed of transition metal species with any suitable ligand. The ATRP system is consisting of the monomer, initiator, and catalyst composed of transition metal species with any suitable ligand. ATRP, which is the most versatile method of the controlled radical polymerization system, uses a wide variety of monomers, catalysts, solvents, and reaction temperature. ATRP is one of the most convenient methods to synthesize well-defined low molecular weight polymers [65].



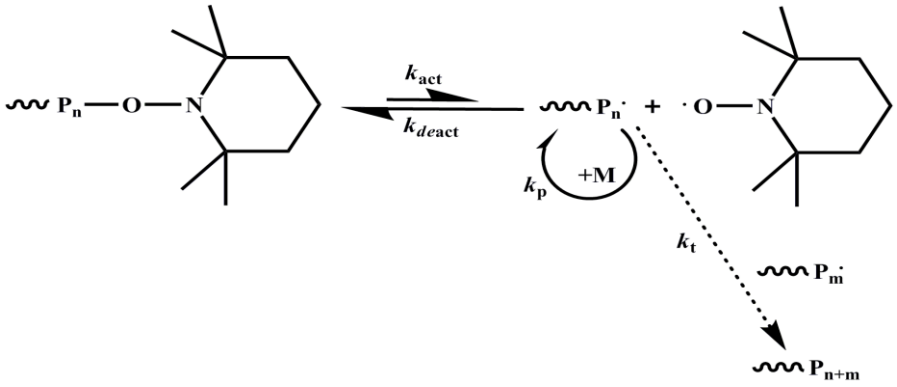
(2.1)

(2.1) represents the general mechanism of ATRP. The radicals the propagating species Pn*, are generated through a reversible redox process catalyzed by a transition metal complex. Radicals react reversibly with the oxidized metal halide complexes, $X–M_t^{n+1}$ / ligand, the deactivator, to reform the dormant species and the activator. These processes are fast, and the dynamic equilibrium that is established favors the dormant species. By this way, all chains can begin growth at the same time, and the concentration of the free radicals is quite low, resulting in reduced amount of irreversible radical-radical termination. Since the deactivation rate constant is substantially higher than that of the activation reaction $K_{eq} = K_{act} / Kd_{eact}$ ~10-7; each polymer chain is protected by spending most of the time in the dormant state, and thereby the permanent termination via radical coupling and disproportionation is substantially reduced. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation, k_p. Termination reactions (k_t)

also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, only several percents of the chains become dead via termination [66]. Polydispersities in ATRP decrease with conversion, with the rate constant of deactivation and also with the concentration of deactivator. The molecular conversion and the amount of initiator used, DP = $\Delta[M]/[I]_0$; polydispersities are low, $M_w / M_n < 1,3$ [67].

2.2.2 Nitroxide-Mediated radical polymerization (NMP)

Nitroxide–mediated radical polymerization (NMP) belongs to a much larger family of processes called stable free radical polymerizations. In this type of process, the propagating species ($P_n°$) reacts with a stable radical (X°) as seen in **(2.2).** The resulting dormant species (P_n-X) can then reversibly cleave to regenerate the free radicals once again. Once $P_n°$ forms it can then react with a monomer, M, and propagate further. The most commonly used stable radicals have been nitroxides, especially 2,2,6,6-tetramethylpiperidinoxy (TEMPO). The 2,2',6,6'-tetramethylpiperidine-1-oxyl radical (TEMPO) was used as the nitroxide component in these initial studies. The alkoxyamine is formed in situ during the polymerization process [72]. Although NMP is one of the simplest methods of living free radical polymerization (LFRP), it has many disadvantages. Many monomers will not polymerize because of the stability of the dormant alkoxyamine that forms. Also, since the reaction is kinetically slow, high temperatures and bulk solutions are often required. Also, the alkoxyamine end groups are difficult to transform and require radical chemistry [73].



(2.2)

The chain end functionalization of polymers synthesized by NMP is a significant problem because dormant chains containing alkoxyamines can regenerate terminal

radicals which can depolymerize at high temperatures. A very interesting chain end functionalization process has also been discovered by Hawker et. al. which involves the controlled monoaddition of maleic anhydride or maleimide derivatives to the alkoxyamine chain end. The alkoxyamine can then be easily eliminated and other functional groups can be introduced [74].

2.2.3 Reversible-Addition fragmentation chain transfer (RAFT)

The most recent report of a controlled/"living" free radical polymerization has been reported by Haddleton and co-workers as well as Thang et al. Reversible addition-fragmentation chain transfer (RAFT) is achieved by performing a free radical polymerization in the presence of dithio compounds, which act as efficient reversible addition-fragmentation chain transfer agents [75].

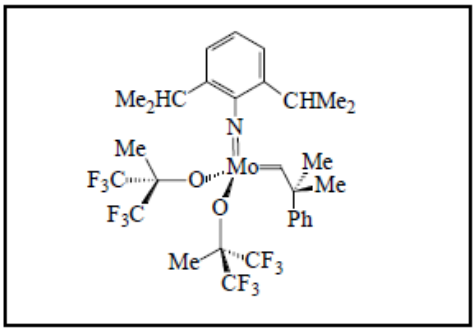
Reversible addition-fragmentation chain transfer (RAFT) incorporates compounds, usually dithio derivatives, within the living polymerization that react with the propagating center to form a dormant intermediate. The dithio compound can release the alkyl group attached to the opposite sulfur atom which can then propagate with the monomer. The greatest advantage to RAFT is the incredible range of polymerizable monomers. As long as the monomer can undergo radical polymerization, the process will most likey be compatible with RAFT. However, there are many major drawback that arise when using this process. The dithio end groups left on the polymer give rise to toxicity, color, and odor and their removal or displacement requires radical chemistry. Also, the RAFT agents are expensive and not commercially available [76].

2.3 Ring-Opening Metathesis Polymerization (ROMP)

Although a relatively new player on the field of polymer chemistry, ring-opening metathesis polymerization (ROMP) has emerged as a powerful and broadly applicable method for synthesizing macromolecular materials. The origins of ROMP can be traced to the mid-1950s when various metals and reagents were combined to uncover new transformations and reactivities involving olefins. However, the rapid rise in popularity and utility of this polymerization technique is the result of extensive work on the identification and isolation of key intermediates involved in the general olefin metathesis reaction. This led to the development of well-defined

ROMP catalysts and ultimately enabled the synthesis of a wide range of polymers with complex architectures and useful functions [16].

It was only in 1971 that a metal-carbene intermediate was proposed by Y. Chauvin, to explain – satisfactorily for the first time – the mechanism. This extraordinary mechanistic proposal, rationalising Chauvin's astonishing new observations, was immediately embraced by the metathesis community and prompted studies on metal-carbene initiators culminating in the creation of the molybdenum- alkylidene catalysts by R. R. Schrock **(2.3)**, and the 1st and 2nd generation of ruthenium-alkylidene catalysts, by R. H. Grubbs **(2.4)** [77].



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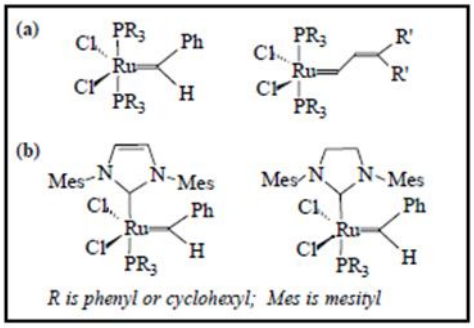
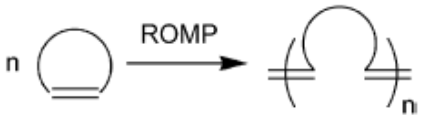


(2.4)

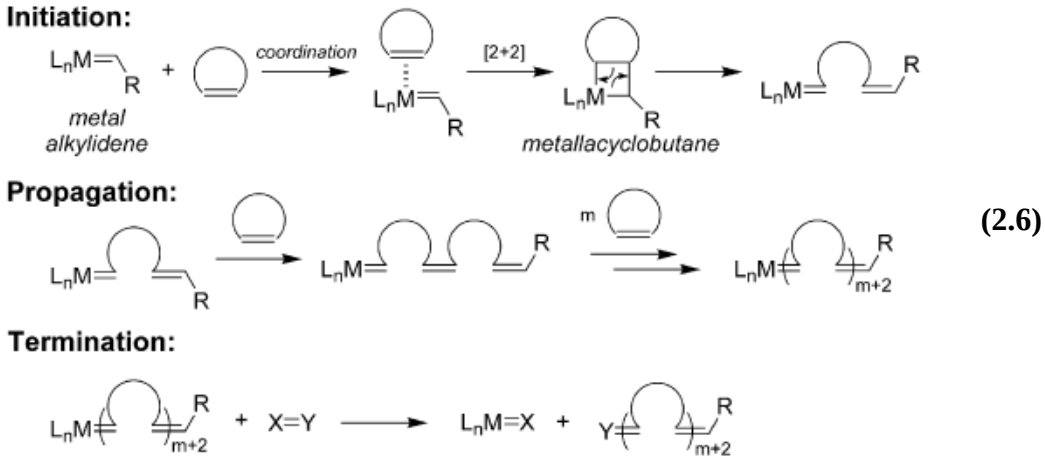
2.3.1 ROMP essentials: mechanism and thermodynamics

The word metathesis comes from the Greek *meta* (change) and *tithemi* (place). In olefin chemistry, it refers to the pair-wise exchange of substituents on a carbon-carbon double bond [78]. Ring-opening metathesis polymerization (ROMP) is a chain growth polymerization process where a mixture of cyclic olefins is converted to a polymeric material **(2.5)**. The mechanism of the polymerization is based on olefin metathesis, a unique metal-mediated carbon‑carbon double bond exchange process. As a result, any unsaturation associated with the monomer is conserved as it is converted to polymer. This is an important feature that distinguishes ROMP from typical olefin addition polymerizations (e.g. ethylene → polyethylene).



(2.5)

Chauvin proposed a general mechanism for ROMP in 1971 [16]. Initiation begins with coordination of a transition metal alkylidene complex to a cyclic olefin **(2.6)**.



(2.6)

After formation of the metal-carbene complex, subsequent [2+2] cycloaddition forms a highly strained metallacyclobutane intermediate. The ring in the intermediate opens to give a new metal alkylidene. The chain growth process proceeds during the propagation stage until all monomer is consumed. Then living ROMP reaction is terminated by adding specialized reagent.

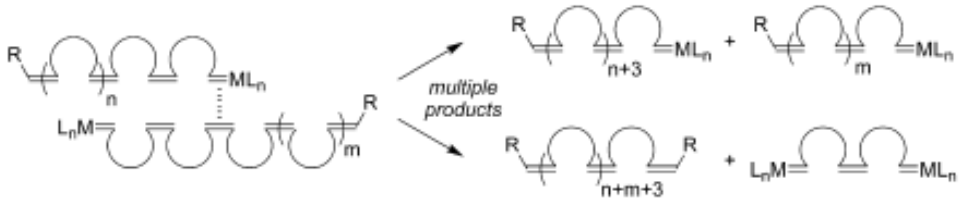
There are three important features regarding metal-mediated ROMP reactions. First, it is important to note that the propagating metal centers on the growing polymer chains may exist in either the metallacyclobutane or metal alkylidene form. This difference depends on the transition metal and its associated ligands, as well as the reaction conditions. Second, like most olefin metathesis reactions, ROMP reactions are generally reversible. Third, although most ROMP reactions are reversible, they are equilibrium-controlled and the position of the equilibrium (monomer vs. polymer) can be predicted by considering the thermodynamics of the polymerization. As with other ring-opening polymerizations, the reaction is driven from monomer to polymer by the release of strain associated with the cyclic olefin (so-called “ring strain”) balanced by entropic penalties. The most common monomers used in ROMP are cyclic olefins which possess a considerable degree of strain (45 kcal/mol) such as cyclobutene, cyclopentene, cis-cyclooctene, and norbornene.

Generally, the most favorable conditions for a successful ROMP reaction is to use the highest monomer concentration at the lowest temperature possible, due to

enthalpic contribution from the relief of ring strain [16].

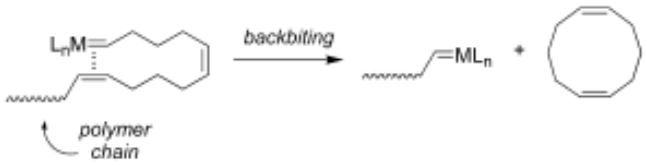
In addition to the general ROMP mechanism illustrated in equation **2.6** (and its related depolymerization mechanism), the equilibria noted above can be established via other metathetical pathways, including intermolecular chain-transfer and intramolecular chain-transfer (so-called "backbiting") reactions. Examples of these types of secondary metathesis reactions are shown in equations **2.7** and **2.8**. In an intermolecular chain-transfer reaction, one polymer chain containing an active metal alkylidene on its terminus can react with any olefin along the backbone of a different polymer chain in the same reaction vessel. Although the total number of polymer chains remains the same, the molecular weights of the individual polymers will increase or decrease accordingly. In a backbiting reaction, the active terminus of a polymer chain reacts with itself to release a cyclic species and a polymer chain of reduced molecular weight. Collectively, these chaintransfer reactions effectively broaden molecular weight distribution (or polydispersity) of the system.

Intermolecular Chain Transfer:



(2.7)

Intramolecular Chain Transfer:



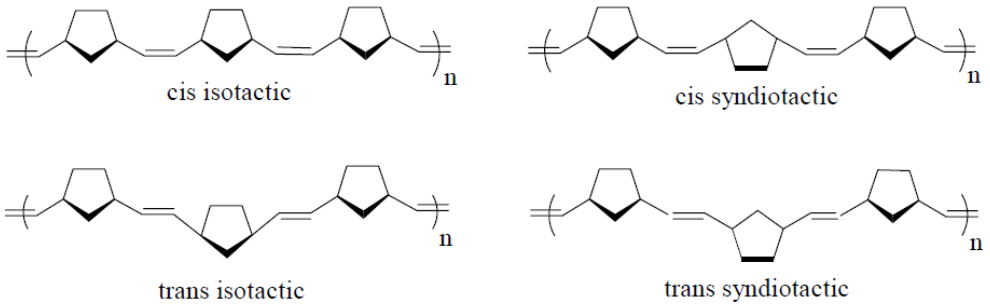
(2.8)

Another implication of equilibrium controlled polymerizations such as ROMP is the propensity to form cyclic oligomers. According to the Jacobson‑Stockmayer theory of ring‑chain equilibria, the formation of cyclic oligomers will always accompany the formation of high molecular weight polymer. The total amount of cyclic species present will depend on factors such as solvent, cis/trans ratio of the polymer backbone, rigidity of the monomer, reaction time, and concentration. Formation of cyclic species is favored at higher temperatures and lower concentrations with a critical value dependent on the factors noted above. While these side reactions challenge the realization of living polymerizations based on ROMP, they can be advantageous. For example, cyclic oligomers can be synthesized in high yields by

simply conducting the ROMP reaction under relatively dilute conditions.

A “living polymerization” was defined by Swarzc as a reaction proceeding without chain transfer or termination. Besides Swarzc’s original concept of the living polymerization, a ROMP reaction requires three more features for its living and controlled reaction. First, the initiation should be fast and complete. Second, there should be a linear relationship between polymer formation and monomer consumption. Third, polymers should be narrowly polydispersed with PDIs<1.5 [16].

ROMP polymers can display a very rich microstructure. Depending on the monomer, three main characteristics can be observed: cis/trans isomerism, tacticity, and head-to-tail bias. Cis/trans isomerism is present in all ROMP polymers and relatively easy to quantify using spectroscopic techniques. Analysis of tacticity has only been successful with polymers made from prochiral monomers **(2.9)**. Head-to-tail bias can be observed with non-symmetrical monomers.



(2.9)

2.3.2 Well-Defined catalysts for ROMP

The studies of two groups deserve particular attention – as recognized by the award of the 2005 Nobel Prize for chemistry to R.H. Grubbs and R.R. Schrock. The award was shared with Y. Chauvin , who was honored for his fundamental studies on metathesis. The investigations of Grubbs and Schrock led to the development of well-defined transition metal alkylidenes that rapidly outrivaled any other initiator or initiation system, particularly those consisting of an often serendipitous mixture of transition metal salts, alcohols and tin alkyls [79].

2.3.2.1 Schrock-type initiators

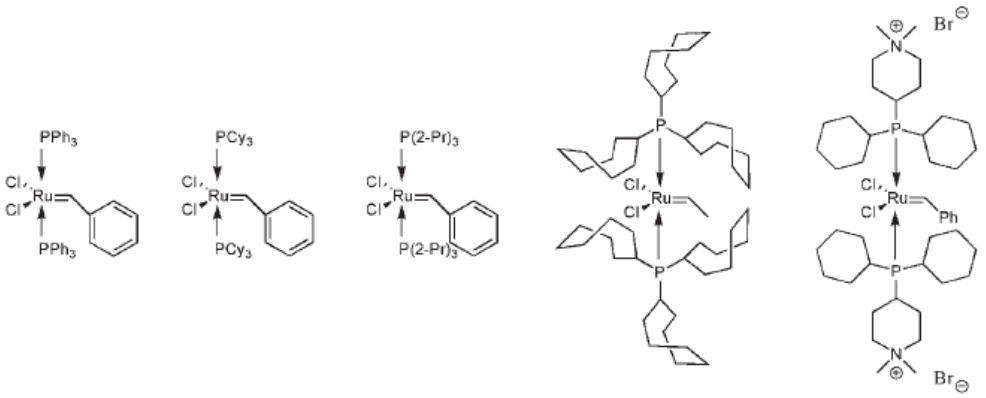
The synthesis of well-defined, high-oxidation state molybdenum alkylidenes was first reported by Schrock and coworkers in 1990 . These, and the analogous tungsten systems, are now commonly named ‘Schrock-catalysts’. The systems possess the

general formula $M(NAr')(OR')_2(CHR).L$, where M= Mo,W; Ar′= phenyl or a substituted phenyl group; R= ethyl, phenyl, trimethylsilyl, CMe_2Ph or t-butyl; R′= CMe_3, CMe_2CF_3, $CMe(CF_3)_2$, $C(CF_3)_2$, aryl, and so on, while L = quinuclidine, trialkylphosphane and tetrahydrofuran (THF) [85].

The Schrock type catalysts are very active and somewhat tolerant with functional groups during ring open metathesis polymerization [80]. In 1993, first chiral molybdenum carbene catalyst was introduced. Then, Schrock and Hoveyda developed more active chiral molybdenum carbene catalyst system, they are so-called the Schrock-Hoveyda catalysts [81].

2.3.2.2 Grubbs-type initiators

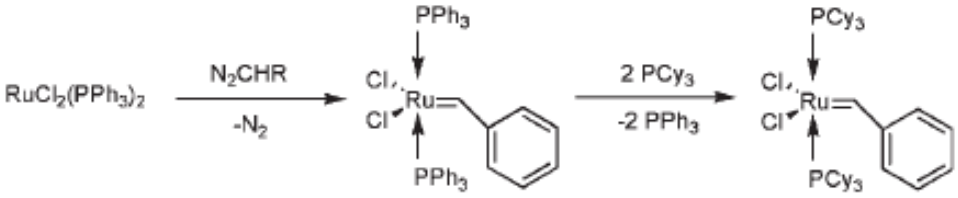
In 1992, Grubbs described the synthesis of the first well-defined ruthenium alkylidene. Thus, the reaction of $RuCl_2(PPh_3)_3$ and $RuCl_2(PPh_3)_4$, respectively, with 2,2-diphenylcyclopropene in benzene or methylene chloride yielded the desired ruthenium carbene complex $RuCl_2(PPh_3)_2(CH=CH=CPh_2)$. As is the case of Schrock-type catalysts, the alkylidene proton in $RuCl_2(PPh_3)_2(CH=CH=CPh_2)$ experiences an agostic interaction with the metal, resulting in downfield NMR shifts for H_α and C_α to δ=17.94 and 288.9 ppm, respectively (both in C_6D_6). Despite a ratio of k_i/k_p <1 (k_p= rate constant of polymerization, k_i= rate constant of initiation), the compound was found to be a quite efficient initiator for the polymerization of norbornene (NBE) and substituted NBEs. The comparably low activity of the bis(triphenylphosphane)-derivative for other cyclic olefins than NBE such as bicyclo [3.2.0]hept-6-ene or trans-cyclo-octene was successfully enhanced by phosphane exchange with more basic analogues, for example tricyclohexylphosphane and tri-(2-propyl)phosphane **(2.10)** [79].



(2.10)

An alternative route to ruthenium alkylidenes that avoided the preparation of 2,2-

diphenylcyclopropene was elaborated by Schwab and Grubbs.The synthetic protocol entailed the reaction of $RuCl_2(PPh_3)_3$ with an diazoalkane **(2.11)** [79].



(2.11)

Via this route, the resulting compounds of the general formula $RuCl_2(PR_3)_2(CHPh)$, (R=Ph, Cy_3)– which today are well known as the first-generation Grubbs catalyst– are accessible in high yields [79].

The Ru-based catalysts have exceptional functional group tolerances compared to other transition metal-based catalysts, especially toward polar functionalities **(Table 2.1)**.

Table 2.1 : Functional group tolerance of early and late transition metal-based ROMP catalysts

Reactivity	Ti/Ta	W	Mo	Ru
↑	acids	acids	acids	**olefins**
	alcohols	alcohols	alcohols	acids
	aldehydes	aldehydes	aldehydes	alcohols
	ketones	ketones	**olefins**	aldehydes
	esters/amides	**olefins**	ketones	ketones
	olefins	esters/amides	esters/amides	esters/amides

The first homogeneous well-defined Ru complex for ROMP was $(PPh_3)_2Cl_2Ru=CH-CH=CPh_2$ [98]. Although this catalyst has a broad range of functional group tolerance and mediates living ROMP reaction with norbornene and cyclobutene monomers, the catalytic activities for other olefines are reduced. To increase the catalytic activities, the bulky and electron-rich phosphine ligands were substituted. The catalysts containing phosphine are tolerant to a broader range of functional groups, such as water and alcohols. However, ROMP reactions of norbornene with the catalyst containing phosphine are not controlled. Because of the different reaction rates between initiation and propagation, the catalyst is not able to provide the desired polymers. Besides, chain transfer reactions occur to yield broadly polydispersed polymers (PDI > 2) [27].

2.3.3 Norbornene: the traditional ROMP monomer

Most common ROMP polymers are derived from norbornene-type monomers. The norbornene structure has recently been used extensively to introduce a variety of functional groups into polymers [83].

Interesting properties are associated with the polynorbornene backbone itself: high glass transition temperature and good thermal stability for example. One disadvantage could be its tendency to easily oxidize in air, but the unsaturation can be removed by hydrogenation.

Also, as compared to other commercial polymerization techniques such as free radical polymerizations, the current ROMP-norbornene system is very attractive. One major problem of radical polymerization is molecular weight control because of chain transfer and termination processes. Controlled/"living" free radical polymerization can be obtained by nitroxyl radical-mediated polymerization and atom transfer radical polymerization (ATRP) [84]. But, those living polymerizations usually require long reaction time for completion. Molecular weight control can also be achieved with living ionic polymerizations but the stringent conditions limit their utility to non-functionalized monomers.

2.4 Ring-Opening Polymerization (ROP)

Ring-opening polymerization (ROP) is a unique polymerization process, in which a cyclic monomer is opened to generate a linear polymer. It is fundamentally different from a condensation polymerization in that there is no small molecule byproduct during the polymerization. Polymers with a wide variety of functional groups can be produced by ring-opening polymerizations. Preparation of cyclic monomers, studies of catalysis and mechanisms are active areas of research both in academia and industry [85-88].

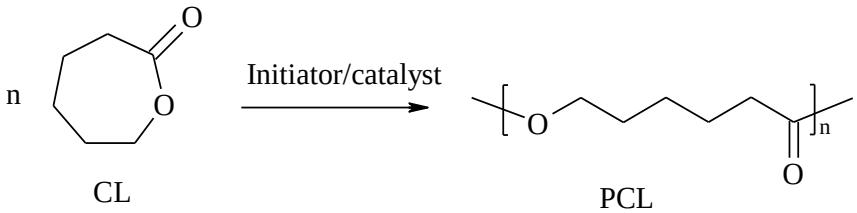
Nowadays, increasing attention is paid to degradable and biodegradable biocompatible polymers for applications in the biomedical and pharmaceutical fields, primarily because after use they can be eliminated from the body via natural pathways and also they can be a solution to problems concerning the global environment and the solid waste management. Aliphatic polyesters are among the most promising materials as biodegradable polymers.

2.4.1 Controlled ROP of cyclic esters

The ring opening polymerization (ROP) of lactones and lactides to produce poly(ester)s provides versatile biocompatible and biodegradable polymers possessing good mechanical properties. These advantages have seen aliphatic poly(ester)s receive increasing attention over the last few years driven by their application as biodegradable substitutes for conventional commodity thermoplastics and applications in the biomedical field [89].

Aliphatic poly(ester)s can be either synthesized by polycondensation of hydroxyl-carboxylic acids or by the ring-opening polymerization (ROP) of cyclic esters. The polycondensation technique yields low molecular weight polyesters (Mn<30.000) with poor control of specific end groups [90]. In contrast, high molecular weight aliphatic polyesters can be prepared in short periods of time by ROP. There has been much research directed towards the controlled ROP of commercially available cyclic esters including glycolide, lactide and ε-caprolactone resulting in aliphatic poly(ester)s with high molecular weights [91].

In practice, the ROP of lactones and lactides requires an appropriate catalyst to proceed in reasonable conditions and to afford polymers with controlled properties **(2.12)**. Since the pioneering work of Kleine et al. in the 1950s metal-based catalytic systems have been the focus of considerable attention for the polymerization of cyclic esters, and numerous studies have been carried out to elucidate the mechanism of such coordination polymerizations. Through variation in the nature of the metal center and of the surrounding ligands, a broad range of initiators have been prepared and evaluated [92, 93, 94, 95].

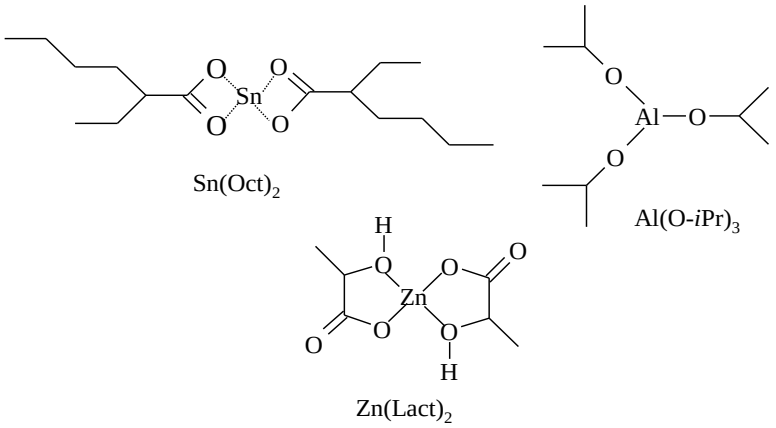


CL PCL **(2.12)**

Besides the coordination-insertion mechanism, alternative strategies based on anionic, nucleophilic, or cationic promoters have also been recently (re)evaluated, the preliminary results reported in these fields being rather promising [96, 97].

2.4.2 Catalysts

A large variety of organometallic compounds, such as metal alkoxides and metal carboxylates, has been studied as initiators or catalysts in order to achieve effective polymer synthesis [93]. The covalent metal alkoxides with free p or d orbitals react as coordination initiators and not as anionic or cationic initiators [98]. The most widely used complex for the industrial preparation of polylactones and polylactides is undoubtedly $Sn(Oct)_2$. It is commercially available, easy to handle, and soluble in common organic solvents and in melt monomers. It is highly active and allows for the preparation of high-molecular-weight polymers in the presence of an alcohol [99]. Aluminum alkoxides have also proved to be efficient catalysts for the ROP of cyclic esters. The common example, namely, aluminum (III) isopropoxide, $Al(Oi\text{-}Pr)_3$, has been largely used for mechanistic studies. However, it has been revealed to be significantly less active than $Sn(Oct)_2$ [100]. Moreover, an induction period of a few minutes is systematically observed with $Al(Oi\text{-}Pr)_3$ attributed to aggregation phenomenon [101]. For all these reasons, $Al(Oi\text{-}Pr)_3$ is much less used for the preparation of biodegradable polyesters, and especially since aluminum ions do not belong to the human metabolism and are suspected of supporting Alzheimer's disease.



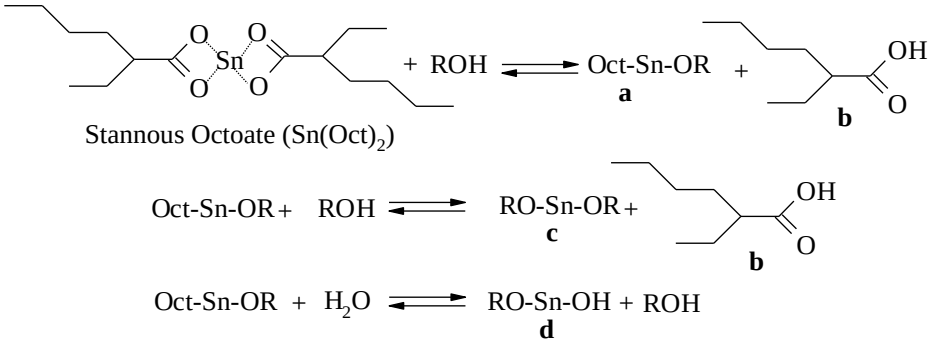
(2.13)

Much interest has thus been devoted to zinc derivatives as potential nontoxic catalysts. Zinc powder itself is a relatively good polymerization catalyst that is used industrially [102]. With reaction times of several days at 140 °C in bulk, it is roughly as active as $Al(Oi\text{-}Pr)_3$. Numerous zinc salts have also been investigated [103].

2.4.3 Coordination-Insertion ROP

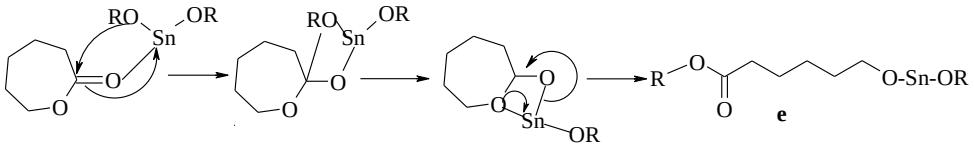
Covalent metal carboxylates, particularly tin(II) bis(2-ethylhexanoate) usually

referred to as tin(II) octanoate, $Sn(Oct)_2$ belong to the most frequently used initiators for polymerization of cyclic esters due to its low cost, low toxicity, and high efficiency. Although, there are controversial reports in the literature about the nature of $Sn(Oct)_2$ activity in the polymerization of lactones, two basic types of mechanism have been proposed. The first one is directly catalytic type where the catalyst serves to activate monomer through coordination with its carbonyl oxygen [104, 105]. The second mechanism is the monomer insertion type mechanism where the catalyst acts as co-initiator along with either purposely added or adventitious hydroxyl impurities, and polymerization proceeds though an activated stannous alkoxide bond [106, 107].



(2.14)

Kricheldorf and co-workers have recently illustrated how the structure of the alcohol initiator may influence the strength of the catalyst/alcohol interaction [105, 107]. According to these authors, this interaction, in the early stages of reaction, is responsible for formation of the "true" initiating species, subsequent ring opening, and formation of the active, propagating chain end. Prior to the beginning of polymerization, adventitious hydroxyfunctional impurities (e.g., water) or purposely added alcohol first complex and subsequently react with $Sn(Oct)_2$ producing a stannous alkoxide species (**a**) and free 2-ethylhexanoic acid (**b**) as shown in **(2.14)**. Further reaction with **a** second equivalent of alcohol produces the stannous dialkoxide initiator (**c**) and releases a second equivalent of 2-ethylhexanoic acid (**b**) as depicted in **(2.14)** [107, 108]. Adventitious water, meanwhile, serves mainly as a catalyst deactivator via a reversible reaction with **a** or **c**, thereby decreasing the concentration of active initiator and producing a stannous alcohol derivative (**d**), such as shown in **(2.14)**, which is more thermodynamically stable than the stannous dialkoxide and is less efficient as an initiator [107].



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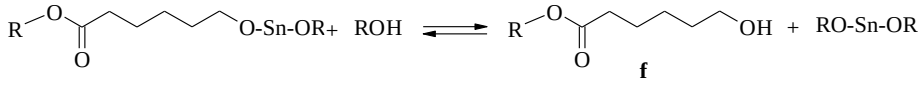


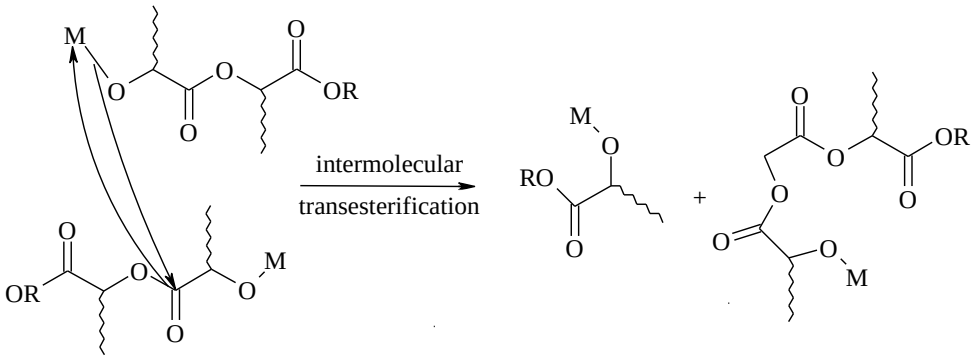
Reaction of **c** with monomer by means of coordination- insertion generates the first actively propagating chain end (**e**) consisting of not only the initiating alcohol fragment but also the active propagating center derived from the first monomer unit and stannous alkoxide. The **e** species may either propagate or undergo rapid intermolecular exchange of the stannous alkoxide moiety for a proton from either hydroxyl groups of initiator (if remaining) or another hydroxy chain end, either **e** or polymeric in nature. This rapid exchange of protons and stannous alkoxide moieties results in a dynamic equilibrium between activated and deactivated chain ends as depicted in **(2.15)**, where R= unreacted alcohol initiator or hydroxy chain ends generated in situ. This process eventually consumes the remaining unreacted alcohol initiator not involved in the initial formation of **c**. ROP based on coordination-insertion mechanism has been thoroughly investigated since it may yield well-defined polyesters through living polymerization [98, 109].

In such coordination-insertion polymerizations the efficiency of the molecular-weight control depends from the ratio $k_{propagation}/k_{initiation}$ but also from the extent of transesterification side reactions. These transesterification reactions can occur both intramolecularly (backbiting leading to macrocyclic structures and shorter chains) and intermolecularly (chain redistributions) **(2.16-2.17)** [110]. Intermolecular transesterification reactions modify the sequences of copolylactones and prevent the formation of block co-polymers. Intramolecular transesterification reactions cause degradation of the polymer chain and the formation of cyclic oligomers.

The polymerization/depolymerization equilibrium should also be taken into account as a particular case of intramolecular transesterification reaction. All of these side reactions result in broader molecular-weight distributions, sometimes making the molecular weights of the resulting polymers irreproducible. The extent of these undesirable transesterification reactions was found to strongly depend on the metallic initiator [100]. Side reactions occur from the very beginning of the polymerization with $Sn(Oct)_2$, leading to rather broad MWD (PDI indexes around 2) but only at high

or even complete conversion with Al(O*i*-Pr)$_3$, yielding lower PDI indexes (less than 1.5) [100, 111].

Parameters that influence the number of transesterifications are temperature, reaction time, and type and concentration of catalyst or initiator. Depending on the metal used, the initiator is more or less active towards transesterification reactions [111].



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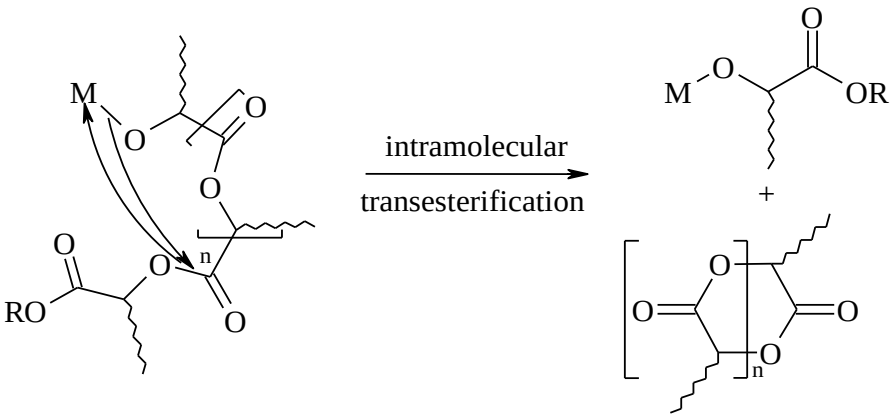


(2.17)

The promising results obtained with Sn(Oct)$_2$, Al(O*i*-Pr)$_3$, and Zn(Lact)$_2$ have given rise to a growing interest in metal-based initiators that would display higher catalytic activity and better control the extent of the undesirable transesterification reactions.

2.4.4 Poly(ε-caprolactone)

Poly(ε-caprolactone) (PCL) is a semicrystalline polymer which represents one of several aliphatic polyesters that undergo degradation and absorbtion in vivo [112, 113]. The repeating molecular structure of PCL homopolymer consists of five non-polar methylene groups and a single relatively polar ester group. Although not produced from renewable raw materials, PCL is a fully biodegradable thermoplastic polymer due to the presence of the hydrolytically unstable aliphatic-ester linkage. PCL has good water, oil, solvent and chlorine resistance.

PCL has some unusual properties, including a low Tg (~ –60 °C) and Tm (~ 60 °C)

and a high thermal stability. These properties are related to PCL's chain of carbons, as longer chains are give rise to less mobility and lower Tm's and Tg's. PCL is also highly permeable, which results from its low Tg and subsequent rubbery state at room temperature.

PCL is one of biodegradable polymers which have been used to prepare functional materials [114]. Copolymers containing poly(ε-caprolactone) (PCL) are especially interesting because they are miscible with a wide range of polymers, and they have features like crystallizability, lack of toxicity, ability to disperse pigments, low-temperature adhesiveness, and printability [115].

PCL has been increasingly studied in the scientific community and applied for drug delivery and tissue engineering [116]. Owing to its high crystallinity and strong hydrophobicity of polymer backbone, PCL homopolymer usually show slow biodegradation and drug-release rate [117].

PCL is compatiable with numerous other polymers, has the possibility of blending this aliphatic polyester with a number of commercial polymers such as poly(vinyl chloride) and bisphenol A polycarbonate. PCL is of interest as a packaging material and in biomedical applications since it is degradable and its degredation products are non-toxic. PCL and other copolymers have been evaluated for medical uses such as drug delivery systems, an external casting material for broken bones, as a material for use in making custom dental impression trays.

In addition to above, it is used mainly in thermoplastic polyurethanes, resins for surface coatings, adhesives and synthetic leather and fabrics. It also serves to make stiffeners for shoes and orthopedic splints, and fully biodegradable compostable bags, sutures, and fibres. Because the homopolymer has a degradation time on the order of 2 years, copolymers have been synthesized to accelerate the rate of bioabsorption. In Sweden there has been an attempt to produce PCL bags, but they degraded before reaching the customers.

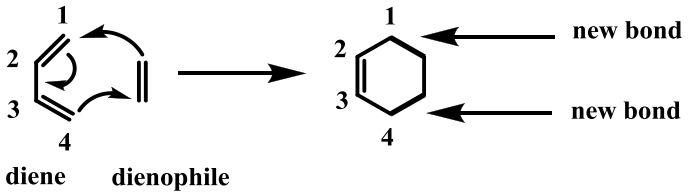
2.5 Click Chemistry

"Click chemistry" is a chemical term introduced by Sharpless in 2001 and describes chemistry tailored to generate substances quickly and reliably by joining small units together [118]. "Click" chemistry can be summarized only one sentence: "Molecules

that are easy to make". Sharpless also introduced some criteria in order to fullfill the requirements as reactions that: are modular, wide in scope, high yielding, create only inoffensive by-products, are stereospecific, simple to perform and that require benign or easily removed solvent. Nowadays there are several processes have been identified under this term in order to meet these criterias such as nucleophilic ring opening reactions; non-aldol carbonyl chemistry; thiol additions to carbon–carbon multiple bonds (thiol-ene and thiol-yne); and cycloaddition reactions. Among these selected reactions, copper(I)-catalyzed azide-alkyne (CuAAC) and Diels-Alder (DA) cycloaddition reactions have gained much interest among the chemists not only the synthetic ones but also the polymer chemists. From this point view, these reactions will shortly be summarized.

2.5.1 Diels-Alder reaction

The Diels-Alder (DA) reaction is a concerted [4π+2π] cycloaddition reaction of a conjugated diene and a dienophile. This reaction is one of the most powerful tools used in the synthesis of important organic molecules. The three double bonds in the two starting materials are converted into two new single bonds and one new double bond to afford cyclohexenes and related compounds **(2.18)**. This reaction is named for Otto Diels and Kurt Alder, who received the 1950 Nobel prize for discovering this useful transformation [119-121].



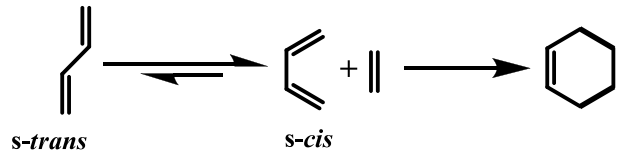
(2.18)

Typically, the DA reaction works best when either the diene is substituted with electron donating groups (like -OR, $-NR_2$, etc) or when the dienophile is substituted with electron-withdrawing groups (like $-NO_2$, -CN, -COR, etc). Many different versions of the DA reaction were elaborated, including intramolecular [4+2] cycloadditions, hetero-Diels-Alder (HDA) reactions, pressure-accelerated DA reactions, and Lewis acid accelerated DA reactions [122].

2.5.1.1 Stereochemistry of Diels-Alder reaction

There are stereochemical and electronic requirements for the DA reaction to occur smoothly. First, the diene must be in an s-*cis* conformation instead of an s-*trans*

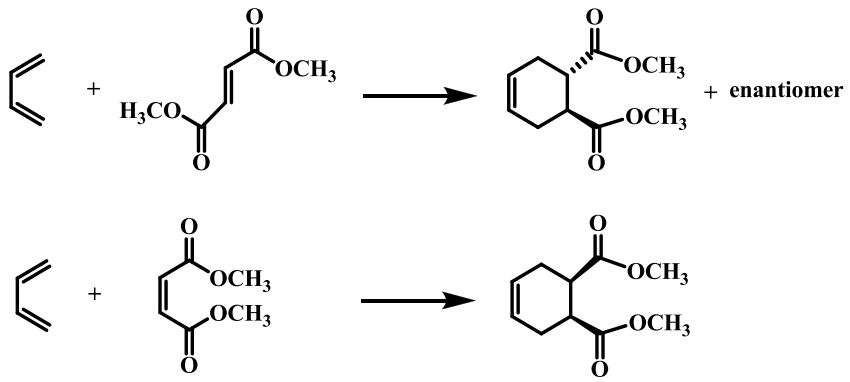
conformation to allow maximum overlap of the orbitals participating in the reaction **(2.19)**.



(2.19)

The "s" in s-*cis* and s-*trans* refers to "sigma", and these labels describe the arrangement of the double bonds around the central sigma bond of a diene. Dienes exist primarily in the lower energy s-*trans* conformation, but the two conformations are in equilibrium with each other. The s-*cis* conformation is able to react in the DA reaction and the equilibrium position shifts towards the s-*cis* conformer to replenish it. Over time, all the s-*trans* conformer is converted to the s-*cis* conformer as the reaction proceeds. Dienes such as cyclopentadiene that are permanently "locked" in the s-*cis* conformation are more reactive than those that are not.

Since the reaction proceeds in a concerted fashion (*i.e.*, bonds are being formed and broken at the same time), substituents that are *cis* on the dienophile will also be *cis* in the product, and substituents that are *trans* on the dienophile will be *trans* in the product **(2.20)** [122-126]:

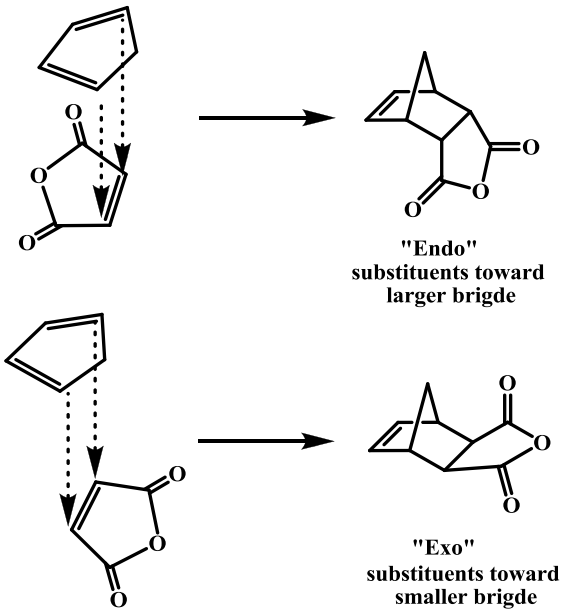


(2.20)

A unique type of stereoselectivity is observed in DA reactions when the diene is cyclic. In the reaction of maleic anhydride with cyclopentadiene, for example, the *endo* isomer is formed (the substituents from the dienophile point to the larger bridge) rather than the *exo* isomer (the substituents from the dienophile point away from the larger bridge) **(2.21)**.

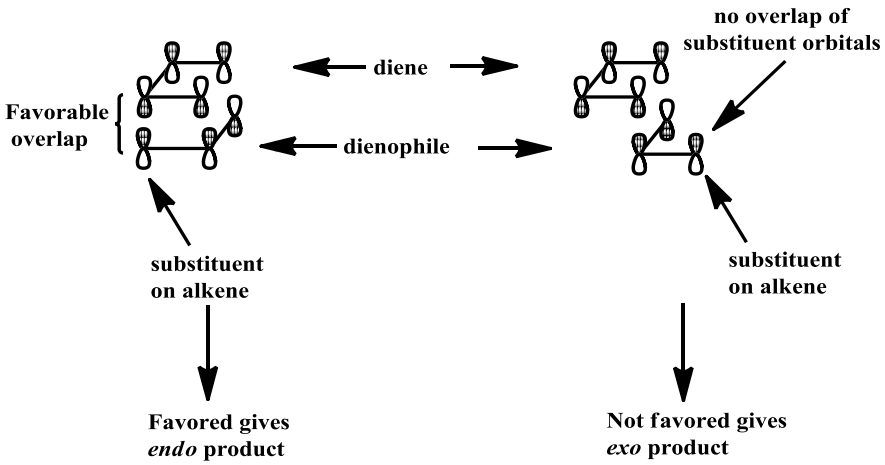
The preference for *endo*–stereochemistry is "observed" in most DA reactions. The fact that the more hindered *endo* product is formed puzzled scientists until

Woodward, Hoffmann, and Fukui used molecular orbital theory to explain that overlap of the *p* orbitals on the substituents on the dienophile with *p* orbitals on the diene is favorable, helping to bring the two molecules together [124,125].



(2.21)

Hoffmann and Fukui shared the 1981 Nobel Prize in chemistry for their molecular orbital explanation of this and other organic reactions. In the illustration below, notice the favorable overlap (matching light or dark lobes) of the diene and the substituent on the dienophile in the formation of the *endo* product **(2.22)**:



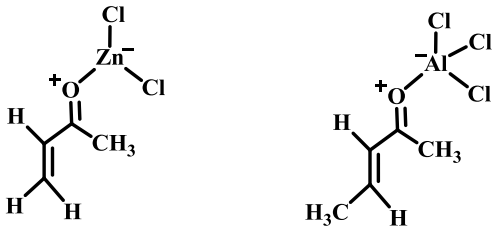
(2.22)

Oftentimes, even though the *endo* product is formed initially, an *exo* isomer will be isolated from a DA reaction. This occurs because the *exo* isomer, having less steric strain than the *endo*, is more stable, and because the DA reaction is often reversible under the reaction conditions. In a reversible reaction, the product is formed, reverts to starting material, and forms again many times before being isolated. The more

stable the product, the less likely it will be to revert to the starting material. The isolation of an *exo* product from a DA reaction is an example of an important concept: thermodynamic *vs* kinetic control of product composition. The first formed product in a reaction is called the kinetic product. If the reaction is not reversible under the conditions used, the kinetic product will be isolated. However, if the first formed product is not the most stable product and the reaction is reversible under the conditions used, then the most stable product will often be isolated.

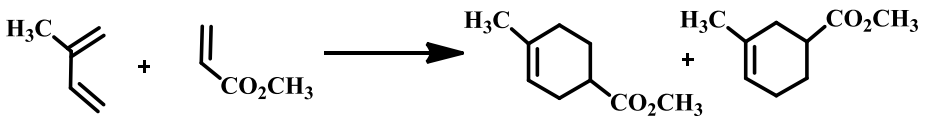
2.5.1.2 Catalysis of diels-alder reactions by lewis acids

The DA reactions are catalyzed by many Lewis acids, including $SnCl_4$, $ZnCl_2$, $AlCl_3$, and derivatives of $AlCl_3$ [122]. A variety of other Lewis acids is effective catalysts. The types of dienophiles that are subject to catalysis are typically those with carbonyl substituents. Lewis acids form complexes at the carbonyl oxygen and this increases the electron-withdrawing capacity of the carbonyl group **(2.23)** [127].



(2.23)

This complexation accentuates both the energy and orbital distortion effects of the substituent and enhances both the reactivity and selectivity of the dienophile relative to the uncomplexed compound [128]. Usually, both regioselectivity and *exo*, *endo* stereoselectivity increases. Part of this may be due to the lower reaction temperature. The catalysts also shift the reaction toward a higher degree of charge transfer by making the electron-withdrawing substituent more electrophilic **(2.24)**.



	"para"	"meta"
Uncatalyzed reaction, 120 ^oC, 6h	70%	30%
$AlCl_3$-catalyzed 20 ^oC, 3h	95%	5%

(2.24)

The solvent also has an important effect on the rate of DA reactions. The traditional

solvents were nonpolar organic solvents such as aromatic hydrocarbons. However, water and other polar solvents, such as ethylene glycol and formamide, accelerate anumber of DA reactions [129-132]. The accelerating effect of water is attributed to "enforced hydrophobic interactions" [130]. That is, the strong hydrogenbonding network in water tends to exclude nonpolar solutes and forces them together, resulting in higher effective concentrations.

2.6 Polymer Topology

The need to synthesize polymers with new and/or improved properties properties has driven the effort to design polymers with novel macromolecular architectures. The properties of polymers depend strongly on their topologies, and finding facile and feasible synthetic methods for polymers with different topological structures remains a goal for polymer chemists. Polymer topology can be generally defined as the fabrication of complex macromolecular structures with defined composition, functionality, and architecture (e.g. telechelic polymers, block copolymers, macromolecular brushes, stars, and networks) as depicted in Figure 2.1.

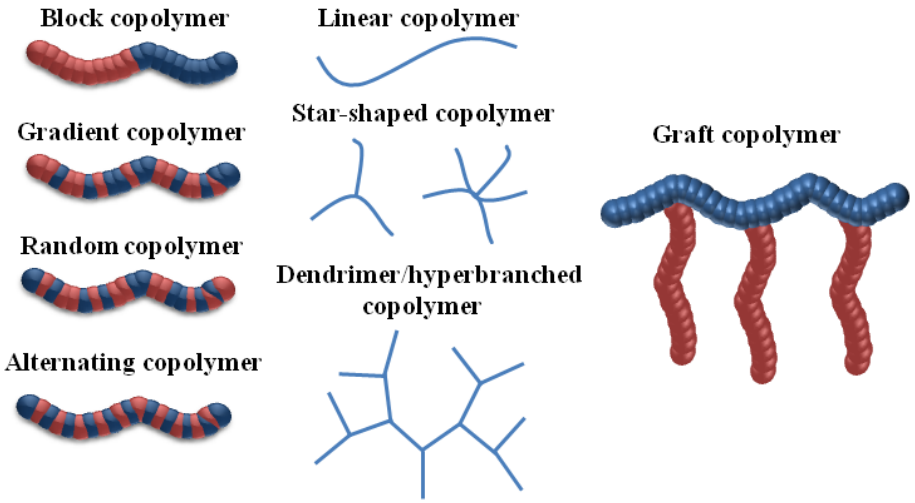


Figure 2.1: Schematic represantation of selected (co)polymer architectures.

C/LRP techniques are well suited for preparation of polymers with precisely controlled architectures, including graft and star polymers as well as branched, dendritic, network, and cyclic type structures. In addition to versatile polymerization chemistry, the synthesis of such complex macromolecules often requires the use of efficient and specific postpolymerization modification techniques to incorporate functionality potentially incompatible with the polymerization conditions and to

build novel structures by coupling preformed polymers. In this respect, click reactions are especially well conformed for such advanced macromolecular design. Indeed, click strategies have served as a complementary tools for most of the major synthetic polymerization techniques, such as ring opening polymerization (ROP), ring opening metathesis polymerization (ROMP), polycondensation, conventional free-radical polymerization, and C/LRPs.

2.6.1 Graft copolymers

Graft polymers refer to the special type of branched polymers in which branched chains are structurally distinct from the main chain. The main chain is commonly called as the backbone and the branches as the side chains which are distributed along the backbones either randomly or uniformly.

When graft polymers characterized by a high density of grafted chains they were named ‘‘macromolecular brushes’’. In terms of chemical composition, macromolecular brushes can be categorized into homopolymer brushes and copolymer brushes. The latter typically consist of two or more types of polymer side chains. When only two types of polymer grafts are involved, they can be arranged in a random, alternating, block, and “centipede” manner.

Graft copolymers have been the subject of continuously increasing interest due to their unique specific properties (morphology, phase behaviour, etc.). In general, graft copolymers can be prepared following three main strategies: (a) the “*grafting onto*”, (b) the “*grafting from*”, and (c) *the* “*grafting through*” strategies which differentiate from each other based on the formation principle. The different pathways are schematically depicted in Figure 2.2 and will be discussed in the context of the ensuing sections.

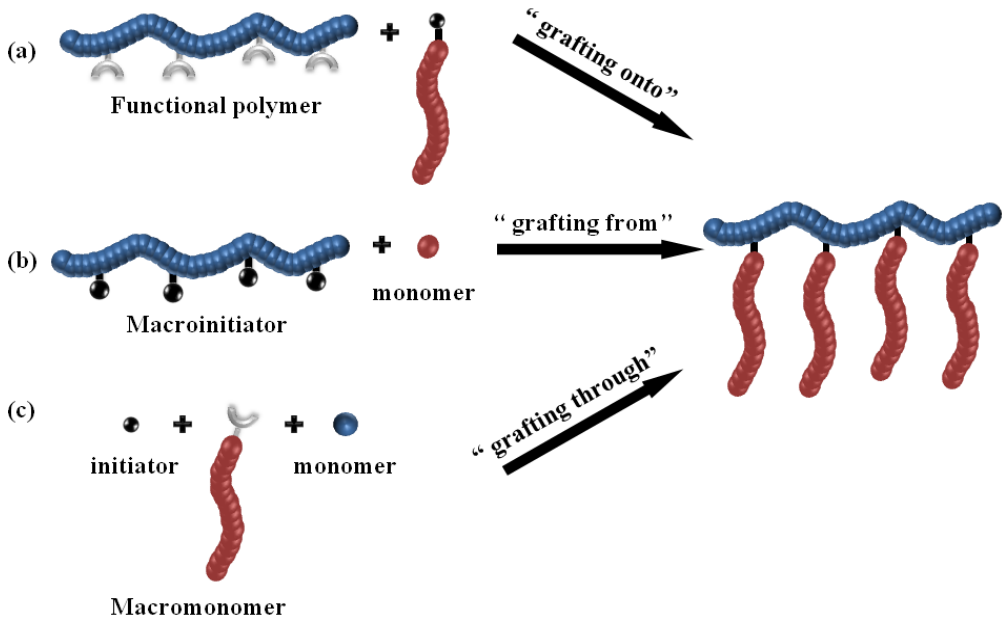


Figure 2.2: Strategies for the synthesis of graft copolymer: (a) ‘‘grafting onto’’, (b) ‘‘grafting from’’, and (c) ‘‘grafting through’’.

The ‘‘*grafting onto*’’ strategy involves the attachment of preformed polymer chains via chemical reaction with reactive side chains of a polymer backbone. Secondly, the ‘‘*grafting from*’’ strategy, consists in a polymerization of the grafts from a polymer backbone bearing initiating sites. The last approach is the ‘‘grafting through’’ strategy which relies on polymerization of appropriate macromonomers.

Each of these strategies controls different structural parameters, including chemical composition, grafting density, degree of polymerization (DP) of side chains, and DP of the backbone. Even though each strategy demonstrates distinct advantages with respect to the molecular design, there are also limitations from a synthetic perspective. There are several strategies that have been employed to synthesize graft polymers thus, increasing interest in their various possible applications. Graft copolymers can be synthesized using any of the various polymerization techniques available including: anionic polymerization, ROMP, conventional radical polymerization, C/LRPs, and various coupling reactions (‘‘click chemistry’’).

2.6.1.1 General synthetic routes

The ‘‘*grafting onto*’’ strategy

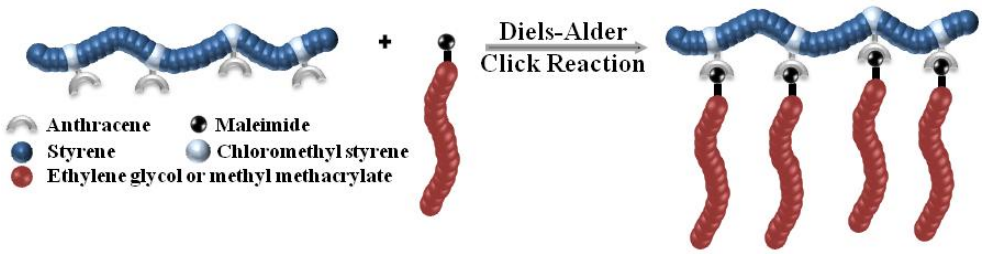
The ‘‘*grafting onto*’’ method (a) relying on grafting of preformed side chains onto a backbone is carried out via a coupling reaction between the pendant functional

groups distributed randomly on the backbone and the complementary end-functional groups of side chains.

The primary advantage of this method is that both backbone and side chains are prepared separately via different living polymerization techniques allowing the more accurate characterization of the resulting polymer with respect to their backbone and side chains. On the other hand, the number of grafted polymer chains is limited due to the steric hindrance and low reactivity of functional groups of the polymer chains resulting in insufficient grafting efficiency.

Usually, ‘‘g*rafting onto*’’ reactions involve the preparation of well-defined side chains by living anionic polymerization and their subsequent reaction with a backbone of monomer units that are susceptible to nucleophilic attack. Examples of such functional groups include esters, anhydrides, benzylic halides, nitriles, chlorosilanes, and epoxides.

In a similar fashion, a Diels-Alder click reaction has been used to prepare graft copolymers. Gacal et al. also applied the “*grafting onto*” approach to the synthesis of graft copolymers containing PS backbone and side chains with either PEG or PMMA units using Diels-Alder click reaction (Scheme 2.25) [133].



(2.25)

The ‘‘*grafting from*’’ strategy

In the “*grafting from*” (b) method, a polymer backbone (macroinitiator) with a predetermined number of initiation sites is generated, followed by grafting the side chains from the macroinitiator. The number of grafted chains can be controlled by the number of initiation sites generated along the backbone assuming that each one participates in the formation of one branch.

The “*grafting from*” approach has been extensively used in the synthesis of well-defined macromolecular grafts and brushes. For instance, PI-*g*-PS and PBd-*g*-PS well-defined copolymers were synthesized several years ago employing anionic polymerization [135,136].

C/LRP techniques are suitable for polymer brush synthesis via grafting from method since low concentration of instantaneous propagating species limit the coupling and termination reactions and the gradual growth of side chains can effectively decrease the steric effect which is inevitable for either ‘‘*grafting-onto*’’ or ‘‘*grafting-through*’’ strategies.

ATRP is a particularly attractive and has been proved to be a highly versatile method to synthesize the graft polymers with well-defined structure including the controllable molecular weight and narrow molecular weight distribution. Matyjaszewski and co-workers have previously described the controlled synthesis of molecular brush copolymers by “*grafting from*” a macroinitiator using ATRP [137].

The ‘‘g*rafting through*’’ strategy

The ‘‘g*rafting through*’’ approach (c) is based on the synthesis of a terminally functional polymer chain followed by a polymerization of this macromonomer.

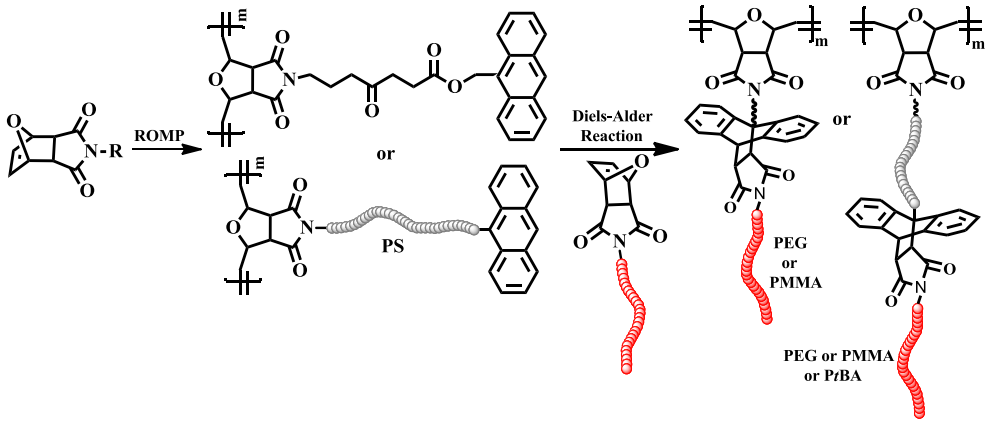
The attractive feature of this method is that the length of side chains and the grafting density can be controlled by adjusting the degree of polymerization of side chains and backbone, respectively. Also, because the macromonomers are prepared separately, the side chains can be characterized prior to polymerization. This method allows preparation of macromolecular brushes with well-defined grafting density and side-chain length. However, the ‘‘g*rafting through*’’ method suffers from the degree of polymerization of the backbone being dependent on the macromonomer length and type. Additionally, due to the necessarily low concentration of polymerizable end groups and high steric hindrance of the propagating chain end, polymerizations can be slow and not proceed to high conversion [138].

The combination of different polymerization approaches such as ROP, ROMP, C/LRP, and living anionic polymerization, “*grafting through*” led to graft copolymers with precisely controlled M_w/M_n, functionality, copolymer composition, backbone length, branch length, and branch spacing.

ROMP has been considered to be an efficient way to synthesize polymacromonomer with complete conversion as well as with a uniform molecular weight distribution since the ring strain and a larger space of ring functional group provide a favorable environment for polymerization.

Recently, Durmaz et al. has reported the synthesis of graft copolymers via combination of ROMP with Diels-Alder click reaction [134]. In this case,

anthracene-functionalized oxanorbornene monomer and oxanorbornenyl PS with ω-anthracene end-functionalized macromonomer were first polymerized via ROMP then coupled with maleimide end-functionalized polymers, including PEG, PMMA, and P*t*BA via Diels-Alder click reaction to create corresponding graft copolymers, as shown in Scheme 2.26.



(2.26)

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3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

Methyl methacrylate (MMA, 99%, Aldrich) and *tert*-butyl acrylate (*t*BA, 99%, Aldrich) were passed through basic alumina column to remove inhibitor and then distilled over CaH_2 in vacuum prior to use. ε-Caprolactone (99%, Aldrich) was distilled from CaH_2 under vacuum. Poly(ethylene glycol monomethyl ether) (M_n = 550, Acros) was dried over anhydrous toluene by azeotropic distillation. *N,N′*-dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Aldrich), CuBr (99.9%, Aldrich), and CuCl (99.9%, Aldrich) were used as received. *N*,*N*,*N′*,*N″*,*N″*-Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) was distilled over NaOH prior to use. Dichloromethane (CH_2Cl_2, 99%, J. T. Baker) was dried and distilled over P_2O_5. Solvents unless specified here were purified by conventional procedures. All other reagents were purchased from Aldrich and used as received without further purification.

3.2 Instrumentation

The ^1H NMR (250 MHz) spectra were recorded on a Bruker NMR Spectrometer in $CDCl_3$. The conventional gel permeation chromatography (GPC) measurements were carried out with an Agilent instrument (Model 1100) consisting of a pump, refractive index (RI), and ultraviolet (UV) detectors and four Waters Styragel columns (guard, HR 5E, HR 4E, HR 3, HR 2), (4.6 mm internal diameter, 300 mm length, packed with 5 μm particles). The effective molecular weight ranges are 2000-4,000,000, 50-100,000, 500-30,000, and 500–20,000, respectively. THF and toluene were used as eluent at a flow rate of 0.3 mL/min at 30 °C and as an internal standard, respectively. The apparent molecular weights ($M_{n,GPC}$ and $M_{w,GPC}$) and polydispersities (M_w/M_n) were determined with a calibration based on linear PS standards using PL Caliber Software from Polymer Laboratories. The second GPC set-up (TD-GPC) with an

Agilent 1200 model isocratic pump, four Waters Styragel columns (guard, HR 5E, HR 4, HR 3, and HR 2), and a Viscotek TDA 302 triple detector including RI, dual laser light scattering (DLLS) (λ = 670 nm, 90° and 7°) and a differential pressure viscometer was conducted to measure the absolute molecular weights ($M_{w,TDGPC}$) in THF with a flow rate of 0.5 mL/min at 35 ^{o}C. Three detectors were calibrated with a PS standard having narrow molecular weight distribution (M_n = 115,000 g/mol, M_w/M_n = 1.02, [η] = 0.519 dL/g at 35°C in THF, dn/dc = 0.185 mL/g) provided by Viscotek company. UV spectra were recorded on a Shimadzu UV-1601 spectrophotometer in CH_2Cl_2.

3.3 Synthesis Methods

4,10-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (**1**), 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (**2)**, 2-bromo-2-methyl propionic acid 2-(3,5-Dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl) ethyl ester (**3**), 4-(2-{[(3-acetyl-7-oxabicyclo[2.2.1]hept-yl)carbonyl]amino} ethoxy)-4-oxobutanoic acid **(4),** 9-anthyrylmethyl 2-bromo-2-methyl propanoate (**5**) and succinic acid mono-anthracen-9-ylmethyl-ester (**6**) were prepared according to published procedures [138-140].

3.3.1 Synthesis of 4,10-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (1)

Maleic anhydride (60.0 g, 0.6 mol) was suspended in 150 mL of toluene and the mixture warmed to 80 °C. Furan (66.8 mL, 0.9 mol) was added via syringe and the turbid solution was stirred for 6 h. The mixture was then cooled to ambient temperature white solids formed during standing were collected by filtration and washed with 2 × 30 mL of petroleum ether and once with diethyl ether (50 mL) afforded **1** as white needless. Yield: 80.2 g (80%). ^{1}H NMR ($CDCl_3$, δ) 6.57 (s, 2H, C*H*=C*H*, bridge protons), 5.45 (s, 2H, -C*H*O, bridge-head protons), 3.17 (s, 2H, C*H*-C*H*, bridge protons).

3.3.2 Synthesis of 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (2)

1 (10.0 g, 60.0 mmol) was suspended in methanol (150 mL) and the mixture cooled to 0 °C. A solution of ethanolamine (3.6 mL, 60 mmol) in 30 mL of methanol was

added dropwise (10 min) to the reaction mixture, and the resulting solution was stirred for 5 min at 0 °C, then 30 min at ambient temperature, and finally refluxed for 6 h. After cooling the mixture to ambient temperature, solvent was removed under reduced pressure, and residue was dissolved in 150 mL of CH2Cl2 and washed with 3 × 100 mL of water. The organic layer was separated, dried over Na2SO4 and filtered. Removal of the solvent under reduced pressure gave white-off solid which was further purified by flash chromatography eluting with ethylacetate (EtOAc) to give the product as a white solid. Yield: 4.9 g (40%). 1H NMR (CDCl3, δ) 6.51 (s, 2H, CH=CH, bridge protons), 5.26 (s, 2H, -CHO, bridge-head protons), 3.74-3.68 (m, 4H, NCH2CH2OH), 2.88 (s, 2H, CH-CH, bridge protons).

3.3.3 Synthesis of 2-bromo-2-methyl-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-en-4-yl) ethyl ester (3)

In a 250 mL of round bottom flask were added **2** (2.0 g, 9.55 mmol) and Et_3N (1.44 mL, 10.54 mmol) in 100 mL of THF. The mixture was cooled to 0 °C, and a solution of 2-bromo isobutyryl bromide (2.34 g, 10.0 mmol) in 25 mL of THF was added dropwise (30 min) to the reaction mixture. The white suspension was stirred for 3 h at 0 °C and subsequently at ambient temperature for overnight. The ammonium salt was filtered off and the solvent was removed under reduced pressure to give a pale-yellow residue that was further purified by column chromatography over silica gel eluting with EtOAc /hexane (1:4) to give **3** as a white solid. Yield: 1.86 g (55%). ^{1}H NMR ($CDCl_3$, δ) 6.49 (s, 2H, C*H*=C*H*, bridge protons), 5.24 (s, 2H, -C*H*O, bridge-head protons), 4.31 (t, *J* = 5.2 Hz, 2H, NCH_2CH_2OC=O), 3.79 (t, *J* =5.2 Hz, 2H, NCH_2CH_2OC=O), 2.85 (s, 2H, C*H*-C*H*, bridge protons), 1.87 (s, 6H, $C(CH_3)_2$-Br).

3.3.4 Synthesis of 4-(2-{[(3-acetyl-7-oxabicyclo[2.2.1]hept-yl)carbonyl]amino} ethoxy)-4-oxobutanoic acid (4)

2 (5 g, 23.9 mmol) was dissolved in 150 mL of 1,4-dioxane. To the reaction mixture were added Et_3N (16.58 mL, 119.6 mmol), DMAP (4.38 g, 35.8 mmol), and succinic anhydride (9.56 g, 95.6 mmol) in that order. The reaction mixture was stirred for overnight at 50 ^{o}C, then poured into ice-cold water and extracted with CH_2Cl_2. The organic phase was washed with 1 M HCl, dried over Na_2SO_4 and concentrated. The crude product was crystallized from ethanol to give **4** as white crystal. Yield: 5.9 g (80%). ^{1}H NMR ($CDCl_3$, δ) 6.50 (s, 2H, C*H*=C*H*, bridge protons), 5.25 (s, 2H, -

C*H*O, bridge-head protons), 4.25 (t, *J* = 5.2 Hz, 2H, $NCH_2CH_2OC=O$), 3.74 (t, *J* =5.2 Hz, 2H, $NCH_2CH_2OC=O$), 2.87 (s, 2H, C*H*-C*H*, bridge protons), 2.66-2.53 (m, 4H, $C=OCH_2CH_2C=OOH$).

3.3.5 Synthesis of 9-anthyrylmethyl 2-bromo-2-methyl propanoate (5)

9-Anthracene methanol (1.50 g, 7.18 mmol) and DMAP (0.175 g, 1.44 mmol) were dissolved in 50 mL of CH_2Cl_2, and Et_3N (1.2 mL, 8.6 mmol) was added. The reaction mixture was then cooled to 0 ^oC. 2-bromo isobutyryl bromide (1.82 g, 7.89 mmol) was added dropwise within 30 minutes to this solution. The reaction mixture was stirred for 15 min. at 0 ^oC then for overnight at room tempeature. The ammonium salt was filtered off and the solvent was evaporated under reduced pressure. The remaining residue was extracted with CH_2Cl_2, and saturated aqueous $NaHCO_3$. The aqueous phase again extracted with CH_2Cl_2, and combined organic phases dried over Na_2SO_4. The solution was concantrated, and the crude product was purified by column chromatography over silica gel eluting with hexane/EtOAc (10:1) to give **5** as yellow solid. Yield: 1.78 g (70%). ^1H NMR ($CDCl_3$, δ) 8.51 (s, 1H, Ar*H* of anthracene), 8.33 (d, *J* = 8.7 Hz, 2H, Ar*H* of anthracene), 8.03 (d, *J* = 8.2 Hz, 2H, Ar*H* of anthracene), 7.60-7.45 (m, 4H, Ar*H* of anthracene), 6.21 (s, 2H, CH_2-anthracene), 1.86 (s, 6H, $C(CH_3)_2$-Br).

3.3.6 Synthesis of succinic acid mono-anthracen-9-ylmethyl-ester (6)

9-Anthracene methanol (4.16 g, 20 mmol) was dissolved in 150 mL of CH_2Cl_2. To the reaction mixture were added Et_3N (14 ml, 100 mmol), DMAP (2.44 g, 20 mmol) and succinic anhydride (8 g, 80 mmol) in that order. The mixture was stirred for overnight at room temperature. After that time, the reaction solution was poured into ice-cold water (150 mL), stirred for 30 min. at room temperature before taking into seperating funnel. The organic phase was extracted with 1M HCl (150 mL). The aqueous phase extracted with CH_2Cl_2 and combined organic phases dried over Na_2SO_4 and concentrated to give **6** as a green solid. Yield: 5.85 g (95%). ^1H NMR ($CDCl_3$, δ) 8.50 (s, 1H, Ar*H* of anthracene), 8.32 (d, *J* = 8.8 Hz, 2H, Ar*H* of anthracene), 8.02 (d, *J* = 8.2 Hz, 2H, Ar*H* of anthracene), 7.60-7.45 (m, 4H, Ar*H* of anthracene), 6.18 (s, 2H, CH_2-anthracene), 2.69-2.62 (m, 4H, $C=OCH_2CH_2C=OOH$).

3.3.7 Synthesis of maleimide end-functionalized PEG (MI-PEG)

Me-PEG (M_n = 550) (2.0 g, 3.63 mmol) was dissolved in 50 mL of CH_2Cl_2. To the reaction mixture were added DMAP (0.044 g, 0.363 mmol) and **4** (2.24 g, 7.27 mmol) in that order. After stirring 5 min at room temperature, a solution of DCC (1.49 g, 7.27 mmol) in 10 mL of CH_2Cl_2 was added. Reaction mixture was stirred for overnight at room temperature. After filtration off the salt, the solution was concentrated and the viscous brown color product was purified by column chromatography over silica gel eluting with CH_2Cl_2/EtOAc mixture (1:1, v/v) and then with CH_2Cl_2/methanol (90:10, v/v) to obtain MI-PEG as viscous brown oil. $M_{n,GPC}$ = 550; M_w/M_n = 1.061 (RI detector, relative to PS standards); $M_{n,theo}$ = 840; $M_{n,NMR}$ =750). ^{1}H NMR ($CDCl_3$, δ) 6.5 (s, 2H, vinyl protons), 5.2 (s, 2H, C*H*C*H*=C*H*C*H*, bridge-head protons), 4.2 (m, 4H, NCH_2CH_2OC=O and C=OOCH_2CH_2), 3.9–3.5 (m, OCH_2CH_2, repeating unit of PEG and NCH_2CH_2OC=O), 3.4 (s, 3H, OCH_3, end group of PEG), 2.8 (s, 2H, CH_2NC=OC*H*-C*H*, bridge protons), 2.6 (m, 4H, OC=OCH_2CH_2C=OO).

3.3.8 General procedure for the synthesis of furan protected maleimide end-functionalized PMMA (MI-PMMA)

In a 25 mL of Schlenk tube, MMA (6.00 mL, 56.1 mmol), PMDETA (0.234 mL, 1.120 mmol), CuCl (0.111 g, 1.120 mmol), toluene (6 mL), and **3** (0.401 g, 1.120 mmol) were added, and the reaction mixture was degassed by FPT cycles, and left in argon. The tube was then placed in a thermostated oil bath at 40 °C for predetermined times. The polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated into hexane. The polymer was dried for 24 h in a vacuum oven at 40 °C. ($[M]_0/[I]_0$ = 50, [I]:[CuCl]:[PMDETA] = 1:1:1, conv. (%) = 40. $M_{n,theo}$ = 2360, $M_{n,NMR}$ = 3250, $M_{n,GPC}$ = 3328, M_w/M_n= 1.298, RI detector, relative to PMMA standards). ^{1}H NMR ($CDCl_3$, δ): 6.5 (s, 2H, vinyl protons), 5.26 (s, 2H, C*H*CH=CHC*H*, bridge-head protons), 4.14 (m, 2H, NCH$_2$CH_2OC=O), 4.0–3.2 (m, OCH$_3$ of PMMA and NCH_2CH$_2$OC =O), 2.9 (s, 2H, CH$_2$NC= OC*H*-C*H*, bridge protons), 2.5– 0.5 (m, CH_2 and CH_3 protons of PMMA).

3.3.9 General procedure for the synthesis of α-furan protected maleimide end-functionalized PtBA (MI-PtBA)

In a 25 mL of Schlenk tube, *t*BA (10.0 mL, 68.3 mmol), PMDETA (0.142 mL, 0.680 mmol), CuBr (0.098 g, 0.68 mmol), ethylene carbonate (0.88 g) and the initiator **3** (0.024 g, 0.68 mmol) were added, and the reaction mixture was degassed by three FPT cycles, and left in argon. The tube was then placed in a thermostated oil bath at 50 °C for predetermined times. The polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst. The excess of THF was evaporated under reduced pressure and the mixture was precipitated into cold methanol/water (80/20; v/v). After decantation, the polymer was dissolved in CH_2Cl_2, extracted with water and the water phase was again extracted with CH_2Cl_2, and combined organic phase was dried over Na_2SO_4. Finally, the organic phase was evaporated to give MI-P*t*BA. The polymer was dried for 24 h in a vacuum oven at 40 °C. ($[M]_0/[I]_0$ = 100; $[I]_0$:[CuBr]:[PMDETA] =1:1:1; conv. (%) = 25. ($M_{n,theo}$ = 3560, $M_{n,NMR}$ = 3700, $M_{n,GPC}$ = 3755, M_w/M_n= 1.188, RI detector, relative to PS standards). ^{1}H-NMR ($CDCl_3$, δ) 6.49 (s, 2H, vinyl protons), 5.2 (s, 2H, C*H*CH=CHC*H*, bridge-head protons), 4.3-4.0 (bs, NCH_2CH_2OC=O and C*H*Br end group of P*t*BA), 3.7 (m, 2H, NCH_2CH_2OC=O), 2.88 (s, 2H, CH_2NC=OC*H*-C*H*, bridge protons), 2.2 (bs, C*H* of P*t*BA), 2.0-1.0 (m, CH_2 and CH_3 of P*t*BA)..

3.3.10 Synthesis of Oxanorbornenyl Anthracene, (6)

Compounds **2** (1.63 g, 7.80 mmol, 1.2 equiv), **5** (2.00 g, 6.50 mmol, 1 equiv), and DMAP (0.400 g, 3.25 mmol, 0.5 equiv) were dissolved in 50 mL of dry CH_2Cl_2. After stirring 5 min at room temperature, DCC (1.6 g, 7.8 mmol, 1.2 equiv) dissolved in 25 mL of CH_2Cl_2 was added to the reaction mixture. The reaction mixture was stirred overnight at room temperature. After filtration, the solvent was removed and the remaining product was extracted with CH_2Cl_2/water. The aqueous phase was again extracted with CH_2Cl_2 and the combined organic phases were dried with Na_2SO_4, and concentrated to dryness. The crude product was purified by column chromatography over silica gel eluting with CH_2Cl_2 to give **6** as a yellow solid (Yield = 2.6 g; 80%). ^{1}H NMR ($CDCl_3$, δ): 8.5 (s, 1H, Ar*H* of anthracene), 8.3 (d, 2H, Ar*H* of anthracene), 8.0 (d, 2H, Ar*H* of anthracene), 7.5 (m, 4H, Ar*H* of anthracene), 6.4 (s, 2H, vinyl protons), 6.1 (s, 2H, CH_2-anthracene), 5.2 (s, 2H, C*H*CH=CHC*H*,

bridge-head protons), 4.2 (t, 2H, $NCH_2CH_2OC=O$), 3.7 (t, 2H, $NCH_2CH_2OC=O$), 2.8 (s, 2H, C*H*-C*H*, bridge protons), 2.6 (s, 4H, $C=OCH_2CH_2C=O$).

3.3.11 Synthesis of Poly(oxanorbornenyl anthracene) via ROMP of 6

The first generation Grubbs' catalyst (PCy3)2(Cl)2-RuCHPh (0.0825 g, 0.100 mmol, 1 equiv.) was placed in a Schlenk tube and dissolved in 2 mL of CHCl3 in a glove box. 3 (1.0 g, 2.00 mmol, 20 equiv.) was dissolved in 8 mL of CHCl3 in another Schlenk tube and added to the catalyst solution via syringe. The flask was capped with a septum and removed from glove box. The polymerization was allowed to stir at room temperature for 2 hours then butyl vinyl ether (1.0 mL) was added to quench the polymerization and stirred additional for 30 min.

Finally, the polymer solution was precipitated in methanol and the obtained polymer was dried for 24 h in a vacuum oven at 40 °C ((6)/catalyst = 20; conv. (%) = 100%; Mn,theo = 10000 ; Mn,GPC = 5752; Mw/Mn = 1.103 (RI detector relative to PS standards). 1H NMR (CDCl3, δ) 8.35 (bs, 1H, ArH of anthracene), 8.23 (bs, 2H, ArH of anthracene), 7.90 (bs, 2H, ArH of anthracene), 7.47 (bs, 2H, ArH of anthracene), 7.24 (bs, 2H, ArH of anthracene), 6.04 (s, 2H, CH2-anthracene), 5.95 (s, 2H, CH═CH, trans), 5.61 (bs, 2H, CH═CH, cis), 4.90 (bs, 2H, ═CH—CH—O, cis), 4.32 (s, 2H, ═CH—CH—O, trans), 4.09 (bs, 2H, C═OOCH2CH2N), 3.54 (bs, 2H, C═OOCH2CH2N), 3.07 (bs, 2H, CH—CH), 2.49 (s, 4H, C═OCH2CH2C═O).

3.3.12 Preparation of Linear Furan-Protected Maleimide PCL (PCL-MI)

PCL-MI was prepared by two step reactions. PCL was prepared by ROP of ε-CL (5.0 mL, 45 mmol) in bulk using tin(II) 2-ethylhexanoate as a catalyst and benzyl alcohol (0.155 mL, 1.5 mmol) as an initiator at 110 °C for 4 h. The degassed monomer, catalyst, and initiator were added to the flamed Schlenk tube equipped with a magnetic stirring bar in that order. The tube was degassed with three FPT cycles, left under argon, and placed in a thermostated oil bath. After the polymerization, the mixture was diluted with THF and precipitated into an excess amount of cold methanol. It was isolated by filtration and dried at room temperature in a vacuum oven at 25 °C for 24 h ($[M]_0/[I]_0$ = 30, $[M]_0/[I]_0$ = 30, conversion (%) = 60; $Mn,_{theo}$ =2150, $Mn,_{NMR}$ =2630, $Mn,_{PCL}$ = 2280, *Mw/Mn* = 1.076, relative to linear PS). ^{1}H NMR (CDCl3, δ): 4.21 (s, 2H, C═CC*H*$_2$O), 4.0 (2H, C*H*$_2$OC═O of PCL),

3.63 (2H, CH2OH, end group of PCL), 2.3 (2H, C═OCH2 of PCL), 1.7–1.3 (6*H*, CH2 of PCL)

Then PCL (1 g, 0.46 mmol) was dissolved in 45 mL of dry CH_2Cl_2. Compound **(4)** (0.71 g, 2.31 mmol) and DMAP (0.056 g, 0.46 mmol) were added to the reaction mixture in that order. After stirring 5 min at room temperature, DCC (0.47 g, 2.31 mmol) dissolved in 5 mL of CH_2Cl_2 was added. Reaction mixture was then stirred at room temperature for 2 hours. Solvent was removed after filtration, and the mixture was precipitated into excess amount of cold methanol. Dissolution/precipitation procedure was repeated two times for the purification of final polymer. The recovered polymer, PCL-MI was dried under vacuum at 25 °C for 24 h ($Mn_{,PCL}$ = 2560; $Mn_{,theo}$ =2450 $Mn_{,NMR}$ =2985, *Mw/Mn* = 1.102, relative to linear PS). ^{1}H NMR ($CDCl_3$, δ) 6.50 (s, 2H, vinyl protons), 5.25 (s, 2H, C*H*CH═CHC*H*, bridge-head protons), 5.09 (s, 2H, C≡CCH_2O), 4.23 (m, 2H, NCH$_2$CH_2OC═O), 4.0 (2H, CH_2OC═O of PCL), 3.73 (m, 2H, NCH_2CH$_2$OC═O), 2.87 (s, 2H, CH$_2$NC═OC*H*—C*H*, bridge protons), 2.56 (s, 4H, C═OCH_2CH_2C═O), 2.3 (2H, C═OCH_2 of PCL), 1.7–1.3 (6H, CH_2 of PCL).

3.3.13 One-Pot Synthesis of Poly(oxanorbornene)-*g*- PMMA-P*t*BA-PMMA via Diels-Alder Reaction

PEG-MI (0.672 g, 0.08 mmol, 8 eq) , PMMA-MI (0.26 g, 0.08 mmol, 8 eq), PtBA-MI (0.296 g, 0.08 mmol, 8 eq) were dissolved in 50 ml of toluene-dioxan mixture. The mixture was bubbled with nitrogen for 30 min and then refluxed for 48 h. The reaction mixture was evaporated under high vacuum. The efficiency of DA reaction was found to be 97% by UV measurement. Next, the reaction mixture was purified by dissolving in THF and then precipitated in methanol. ^{1}H NMR ($CDCl_3$, δ) 7.0-7.5 (Ar*H*), 6.05 (C*H*=C*H*, trans), 5.7 (C*H*=C*H*, cis), 5.4 (CH_2-adduct), 5.1 (=CH-C*H*-O, cis), 4.7 (CH, bridge head protons), 4.4 (=C*H*-C*H*-O, trans), 4.2 (C=OOCH_2CH_2N), 4.0-3.0 (OCH_2CH_2 of PEG, OCH_3 of PMMA, C=OOCH_2CH_2N, C*H*-C*H*, C=OOCH_2, OCH_3 of PEG), 2.5 (C=OCH_2CH_2C=O of PEG and C=OCH_2CH_2C=O), 2.2 (C*H* of PtBA), 2.0-1.0 (CH_2 and CH_3 of PMMA).

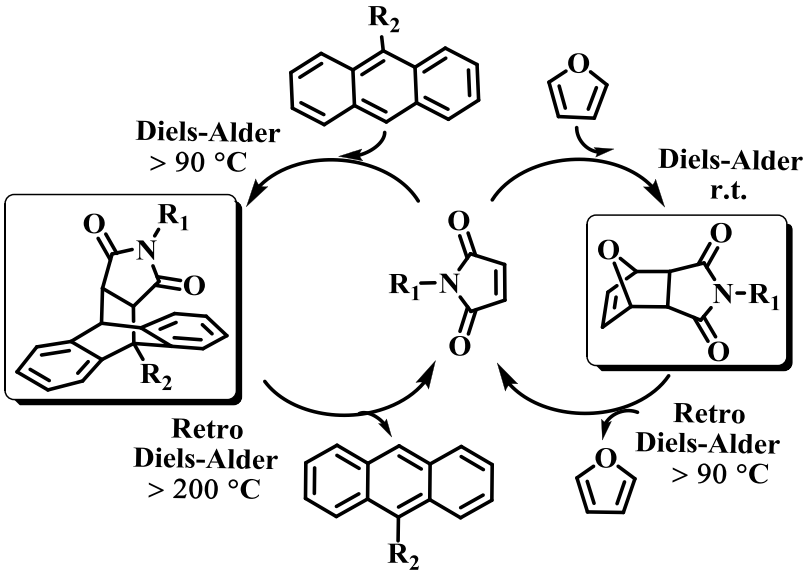
3.3.14 One-Pot Synthesis of Poly(oxanorbornene)-g- PEG-PCL-PMMA via Diels-Alder Reaction

PEG-MI (0.672 g, 0.08 mmol, 8 eq) PMMA-MI (0.26 g, 0.08 mmol, 8 eq), PCL-MI

(0.211 g, 0.08 mmol, 8 eq) were dissolved in 50 ml of toluene-dioxan mixture. The mixture was bubbled with nitrogen for 30 min and then refluxed for 48 h. The reaction mixture was evaporated under high vacuum. The efficiency of DA reaction was found to be 98% by UV measurement. Next, the reaction mixture was purified by dissolving in THF and then precipitated in methanol. ^{1}H NMR ($CDCl_3$, δ) 7.0-7.5 (Ar*H*), 6.05 (C*H*=C*H*, trans), 5.7 (C*H*=C*H*, cis), 5.4 (CH_2-adduct), 5.1 (=CH-C*H*-O, cis and C=CCH_2O of PCL), 4.7 (CH, bridge head protons), 4.4 (=C*H*-C*H*-O, trans), 4.2 (C=OOCH_2CH_2N), 4.0 (CH_2OC=O of PCL), 4.0-3.0 (OCH_2CH_2 of PEG, OCH_3 of PMMA, C=OOCH$_2$CH_2N, C*H*-C*H*, C=OOCH_2, OCH_3 of PEG), 2.6 (C=OCH_2CH_2C=O of PEG and C=OCH_2CH_2C=O), 2.3 (C=OCH_2 of PCL), 2.0-1.0 (CH_2 and CH_3 of PMMA) and 1.7–1.3 (CH_2 of PCL).

4. RESULTS AND DISCUSSION

Using a combination of ROMP-Diels-Alder reaction strategies enabled us to prepare graft copolymers with a new versatile method. Therefore, it was tested whether Diels-Alder reaction was sufficient to form graft copolymers with maleimide end-functionalized polymers and preparing them in a one-pot. The strategy that we followed during this thesis is based on a DA reaction between anthracene and maleimide end-functionalized polymers. The whole synthetic pathways during this thesis can be summarized as the following equation (4.1).

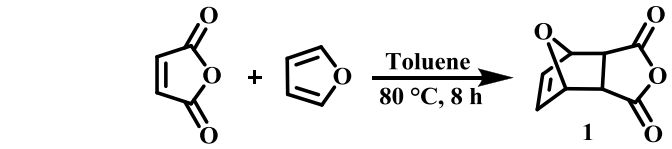


(4.1)

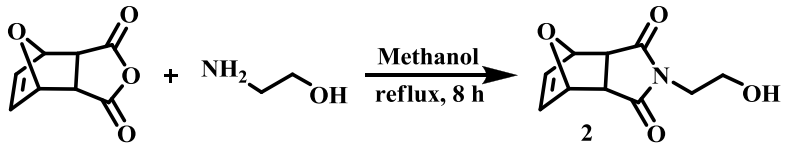
First, furan protected maleimide polymers are prepared by ATRP, ROP and esterification reactions. Then protected maleimide end-functionalized prepolymers are deprotected by retro Diels-Alder (r-DA) by heating at 110 ^{o}C in toluene. The recovered maleimide groups are added irreversibly to anthryl functional polymers *in situ* to undergo the DA reaction in order to obtain anthracene-maleimide adduct.

4.1 Synthesis of Copolymers

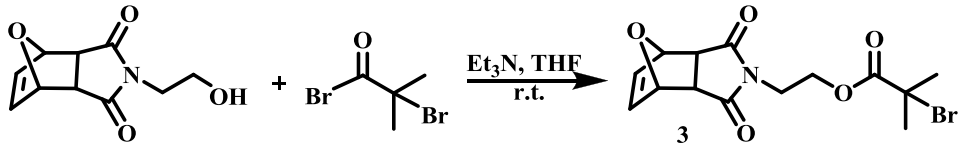
The initiators with proper functionalities for DA reaction were first prepared. 2-bromo-2-methyl-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-en-4-yl) ethyl ester (3) was first synthesized within three steps. Furan and maleic anhydride were reacted in toluen at 80 ^{o}C, then the formed adduct (1) (4.2), was utilized for the synthesis of 2 by adding the solution 2-amino ethanol in methanol into dispersion of 1 in methanol (4.3). Finally, 3, was obtained via an esterification reaction between 2 and 2-bromoisobutryl bromide in THF at room temperature (4.4).



(4.2)



(4.3)



(4.4)

From overlay 1H NMR spectra of 3 as seen in Figure 4.1, it was clearly seen that the methyl protons next to Br were detected at 1.87 ppm and the methylene protons next to the ester unit at 4.31 ppm. Moreover, the characteristic protons of the adduct were also detected at 6.49 ppm (bridge vinyl protons), 5.24 ppm (bridge-head protons) and 2.85 ppm (bridge protons) respectively. These results confirmed that the synthesis of 3 was achived.

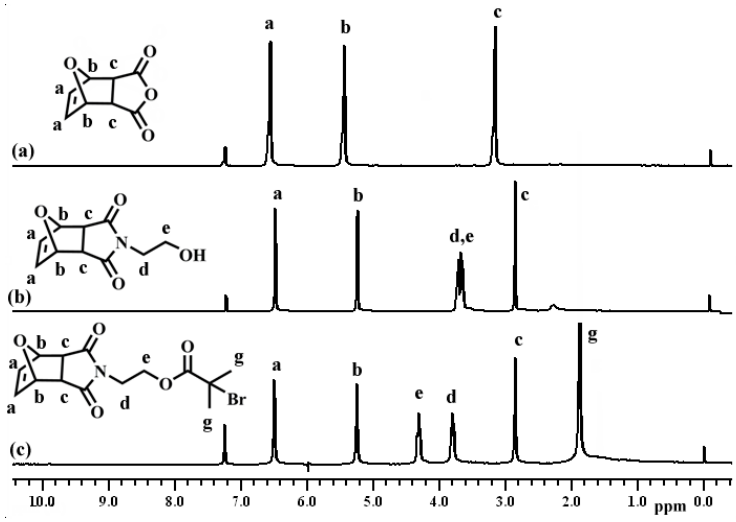
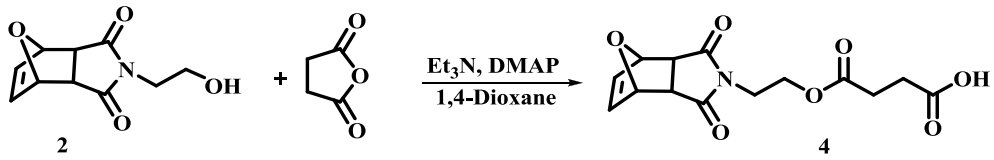


Figure 4.1: ^{1}H NMR spectra of: a) 3-acetyl-N-(2-hydroxyethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid (1); b) 3-acetyl-N-(2-hydroxyethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxamide (2); c) 2-bromo-2- methyl-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-en-4-yl) ethyl ester (3) in $CDCl_3$.

The hydoxyl functionality of **2** was converted to carboxylic acid via a reaction with succinic anhydride in the presence of Et_3N/DMAP catalyst system and 1,4-dioxane as solvent in order to give **4. (4.5)**



(4.5)

From ^{1}H NMR spectrum as seen in Figure 4.3 of **4**, methylene protons next to the ester ($NCH_2CH_2OC{=}O$) and methylene protons adjacent to nitrogen ($NCH_2CH_2OC{=}O$) appeared at 4.25 ppm and 3.74 ppm respectively. Moreover, the multiplet peaks around 2.66-2.53 ppm confirmed successful conversion of hydroxyl group to carboxylic acid.

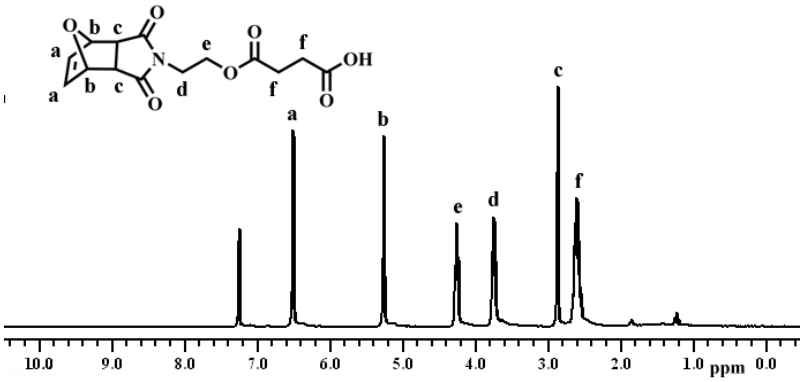
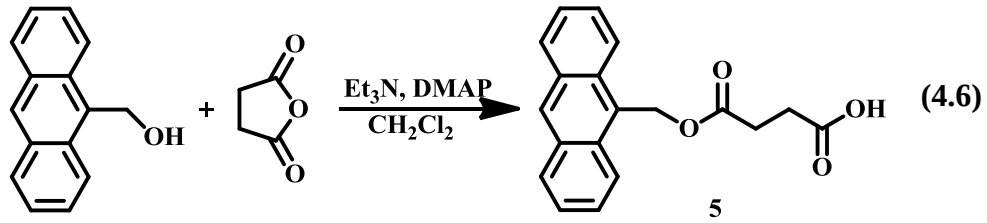


Figure 4.2: ^{1}H NMR spectrum of 4-(2-{[(3-acetyl-7-oxabicyclo[2.2.1]hept-yl)carbonyl]amino}ethoxy)-4-oxobutanoic acid (4) in $CDCl_3$.

A similar procedure was applied to the synthesis of 5. In this case, 9-anthracene methanol was used as starting material **(4.6)**.



(4.6)

5

Again, the structure was confirmed by ^{1}H NMR spectrum as seen in Figure 4.3. A shift from 5.6 ppm to 6.18 ppm of methylene protons linked to anthracene ring due to esterification reaction and multiplet peaks around 2.69-2.62 ppm aasigned to C=OCH_2CH_2OC=O clearly indicated that **5** was achieved.

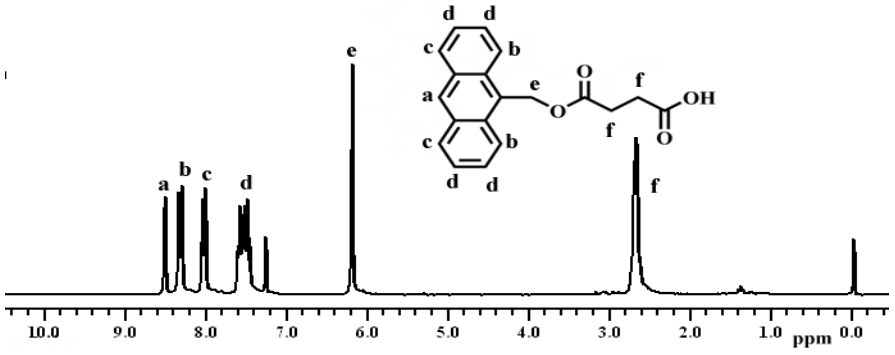
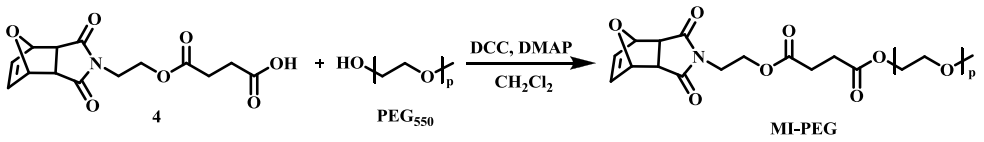


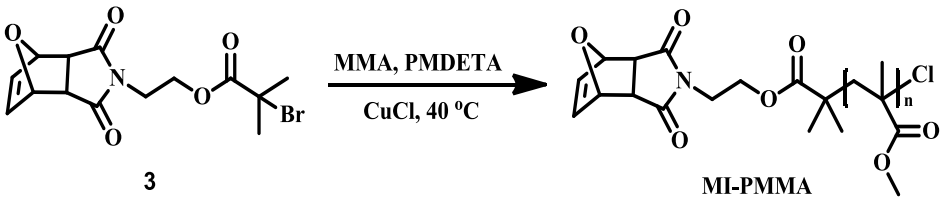
Figure 4.3: ^{1}H NMR spectrum of succinic acid mono-anthracen-9-ylmethyl-ester (5) in $CDCl_3$.

Before ATRP of the precursor polymers, condensation reaction of PEG precursors was carried out. MI-PEG was obtained as brown oil after esterification reaction between **4** and Me-PEG (550) **(4.7)**. From ^{1}H NMR spectrum of the polymer, the bridge and bridge-head protons were detected at 6.5, 5.2 and 2.8 ppm respectively. The $M_{n,NMR}$= 750 of MI-PEG was determined from a ratio of integrated peaks at 3.62 ppm (OCH_2CH_2 protons of PEG) to 6.5 ppm (vinyl end protons).

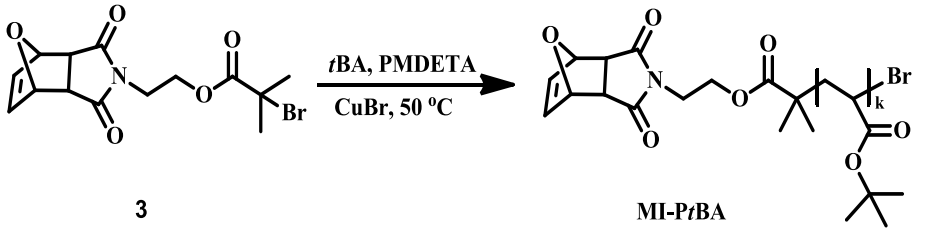


(4.7)

Next, MI-PMMA **(4.8)** and MI-P*t*BA **(4.9)** were obtained by ATRP of MMA and *t*BA using **3** as initiator. Since furan protection was easily deprotected at elevated temperatures, the polymerization temperature for *t*BA and MMA were purposely kept low in order to prevent possible copolymerization of maleimide and monomers during polymerization. Number-average molecular weight calculated by GPC ($M_{n,GPC}$) of MI-PMMA and MI-P*t*BA were in fairly good agreement with the theoretical one ($M_{n,theo}$) indicating that the initiations were not quantitative under these polymerization conditions.



(4.8)



(4.9)

The $M_{n,NMR}$ of MI-PMMA and MI-P*t*BA were determined from a ratio of integrated peaks at 3.58 ppm (OCH_3 protons of MMA) and 2.2 ppm (C*H* protons of P*t*BA) to 6.5 ppm (vinyl end protons). Molecular weight of **3** was added to this value. $M_{n,NMR}$ values were consistent with those of the $M_{n,GPC}$ (Table 4.1). From Table 4.1. It was found good agreement between $M_{n,theo}$ $M_{n,NMR}$ and $M_{n,GPC}$ values.

Polymer	Ini.	Time (min)	Conv.[c] (%)	$M_{n,GPC}$[d] (g/mol)	M_w/M_n	$M_{n,theo}$[e] (g/mol)	$M_{n,NMR}$ (g/mol)
MI-PMMA[a]	**3**	30	40	3330[d]	1,29	2360	3250
MI-P*t*BA[b]	**3**	90	25	3755[d]	1,18	3560	3700

Table 4.1: Polymers obtained from ATRP

[a] $[M]_0:[I]_0:[CuCl]:[PMDETA]$ = 50:1:1:1; polymerization was carried out at 40 °C. MMA / toluene = 1 (v/v).

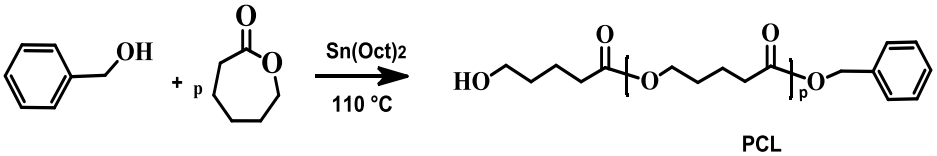
[b] $[M]_0:[I]_0:[CuBr]:[PMDETA]$ = 100:1:1:1; polymerization was carried out at 50 °C. *t*BA / EC = 10 (w/w).

[c] Determined by gravimetrically.

[d] Molecular weigths were calculated according to linear PS standards.

[e] $M_{n,theo}$ = ($[M]_o/[I]_o$) X conversion % X MW of monomer + MW of initiator.

After ATRP reactions, PCL was synthesized by ROP of ε-CL in bulk using tin(II) 2-ethylhexanoate as a catalyst and benzyl alcohol as an initiator.



(4.10)

$M_{n,GPC}$ of PCL is calculated as 4745 relative to PS standards.. But it is corrected according to the equation $M_{n,PCL} = 0.259 \text{ X } M_{n,GPC}^{1.073}$ ($M_{n,PCL}$ = 2280).

$M_{n,NMR}$ was determined by using the following equation: $M_{n,NMR}$ = DP_n of PCL + MW of ε-CL + MW of initiator = 22 X 114.1 + 108 = 2600

$M_{n,theo}$ = ([M]o/[I]o) X conversion % X MW of monomer + MW of initiator= 2200

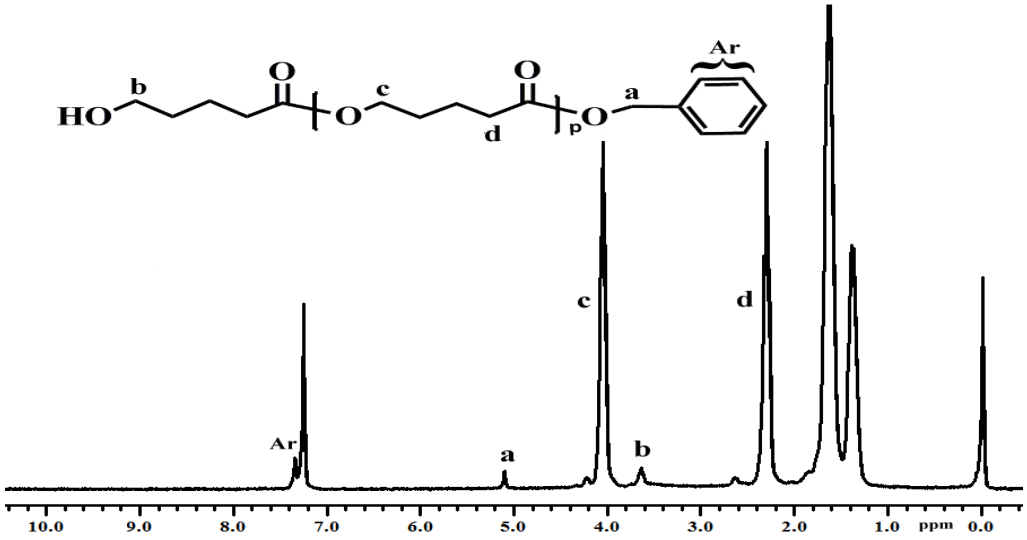


Figure 4.4: ^{1}H NMR spectrum of PCL in $CDCl_3$

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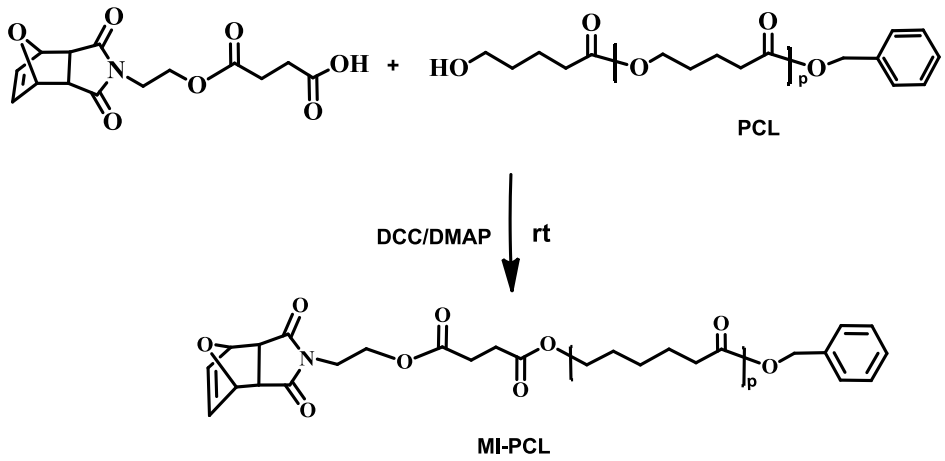
Linear Furan-Protected Maleimide functionalized PCL (PCL-MI) was obtained after esterification reaction between **4** and PCL.



(4.11)

$M_{n,GPC}$ of PCL-MI is calculated as 5295 relative to PS standards.. But molecular weight is corrected according to the equation $M_{n,PCL} = 0.259 \text{ X } M_{n,GPC}^{1.073}$ ($M_{n,PCL}$ =

2560 ; $Mn_{,theo}$ =2450 $Mn_{,NMR}$ =2900, *Mw/Mn* = 1.102, relative to linear PS) A good agreement was found between $M_{n,NMR}$, $M_{n,theo}$, and $M_{n,PCL}$.

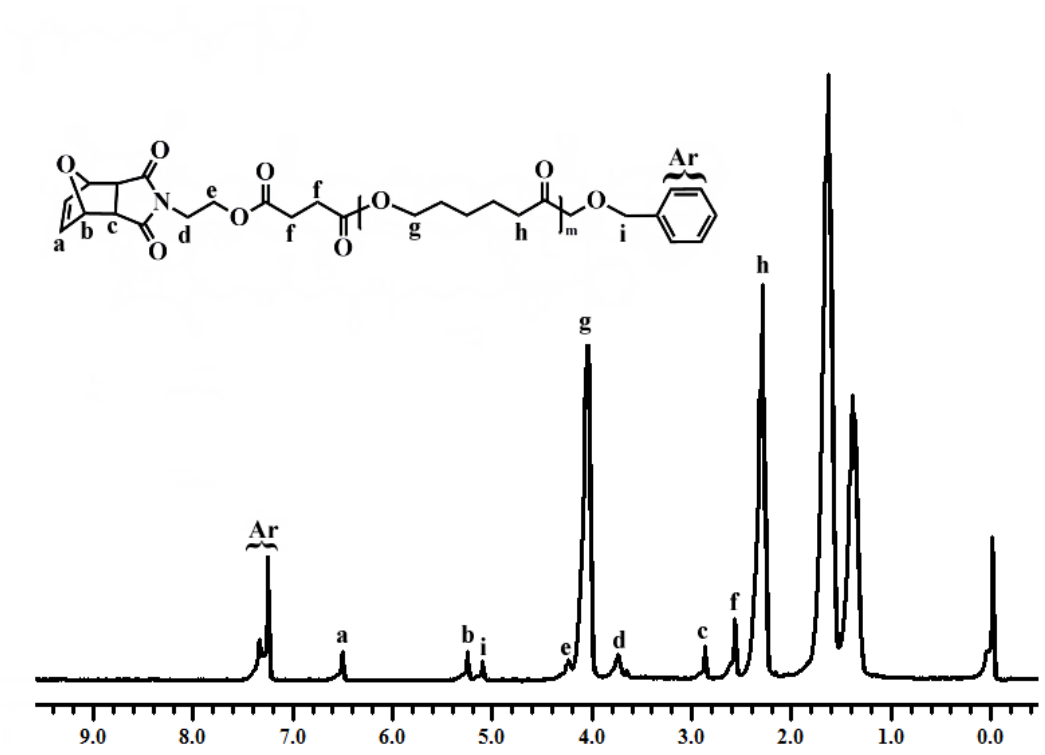
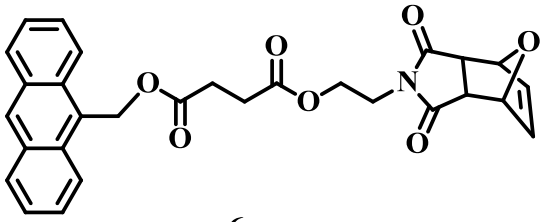


Figure 4.5: ^{1}H NMR spectrum of PCL-MI in $CDCl_3$

4.2 Preparation of Graft Copolymers via Combination of ROMP and Diels-Alder Reaction

Anthracene-functionalized oxanorbornene (oxanorbornenyl anthracene) monomer **6** was synthesized via esterification reaction of **2** and **5** catalyzed by DCC and DMAP in CH_2Cl_2 at room temperature overnight **(4.12)**.

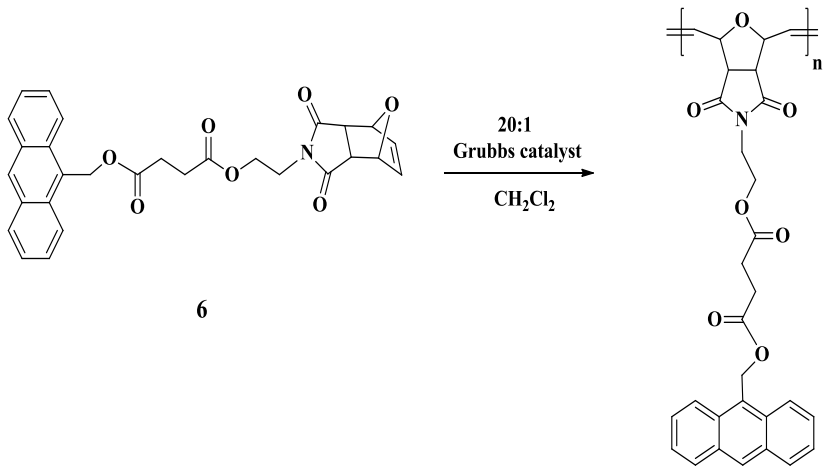


(4.12)

6

1H NMR spectroscopy confirmed clearly the structure of 6 by appearance of characteristic signals of anthracene (δ 8.5-7.5) and vinyl protons (δ 6.4). Next,

poly(oxanorbornenyl anthracene) was obtained via ROMP of 7 using the first generation Grubbs' catalyst (PCy3)2(Cl)2-RuCHPh in CH2Cl2 at room temperature for 20 min, followed by a reaction with butyl vinyl ether as a terminating agent for additional 20 min (4.13).



6

poly(oxanorbornenyl anthracene)

(4.13)

GPC and 1H NMR spectroscopy confirmed that poly(oxanorbornenyl anthracene) was appropriately prepared with controlled molecular weight, low polydispersity index (PDI) and desired anthracene pendant groups. The number-average theoretical molecular weight (Mn,theo = 10000), which did not fit with the number-average molecular weight by conventional GPC ($M_{n,GPC}$ = 5755) relative to linear PS standards was comparable to that obtained from three detection GPC ($M_{n,TDGPC}$ = 11200). In the NMR spectrum, the shift of the vinyl protons (6.04 ppm) to the 5.9 (C*H*=C*H*, trans) and 5.6 ppm (C*H*=C*H*, cis) was observed upon the ROMP of **6**,

which revealed that poly(oxanorbornenyl anthracene) had occurred as seen in Figure 4.4.

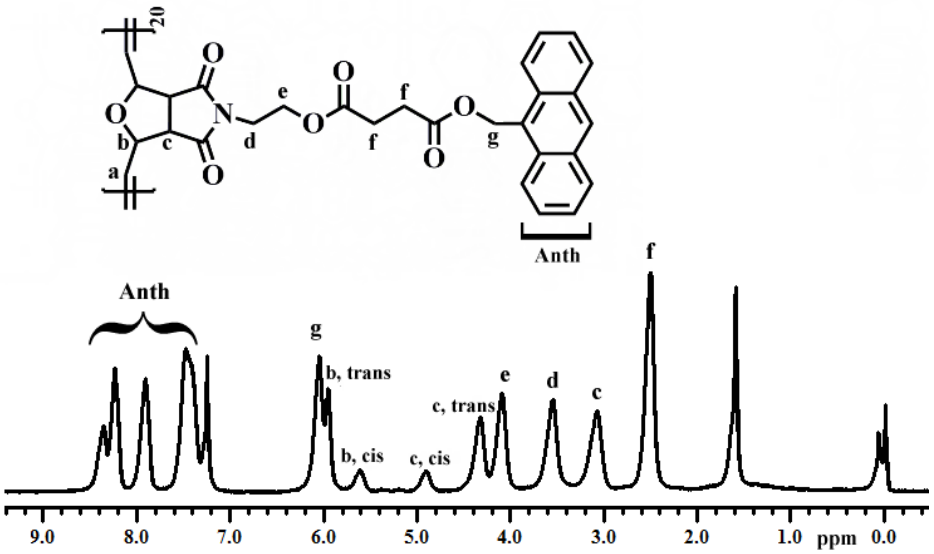
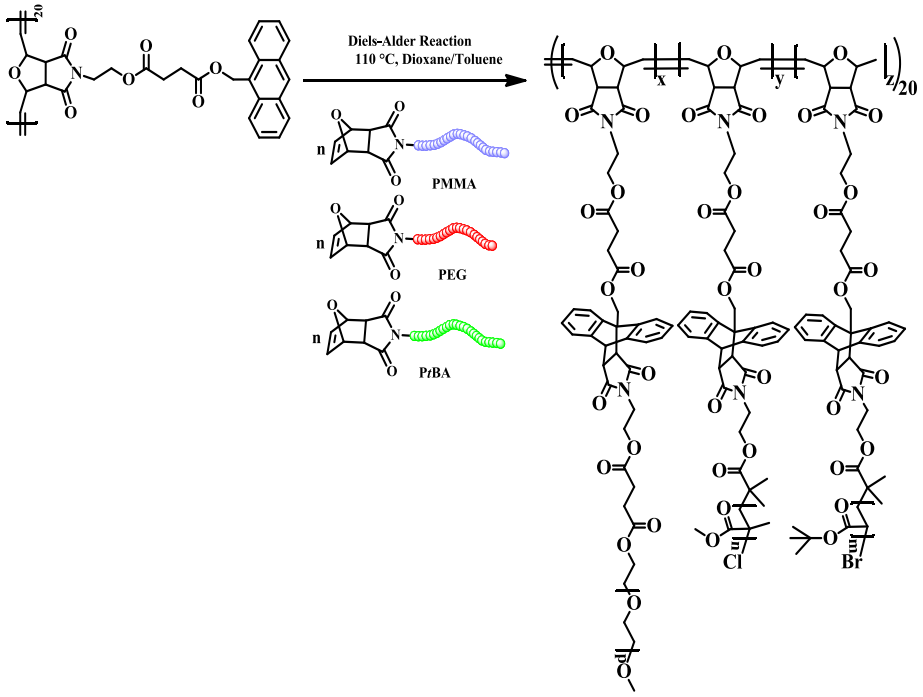


Figure 4.6: ^{1}H NMR spectrum of poly(oxanorbornenyl anthracene) in $CDCl_3$

Next, same equivalent (8 eq) of PEG-MI, PMMA-MI and P*t*BA-MI were grafted to poly(oxanorbornenylanthracene) via Diels-Alder reaction to yield poly(oxanorbornene)-*g*-PEG-PtBA-PMMA **(4.14)**.



(4.14)

8 equiv of PMMA, 7 equiv of PEG and 5 equiv of P*t*BA per anthracene unit were employed in Diels-Alder reaction, because of the DP_n of the poly(oxanorbornenyl anthracene) was calculated to be 20 based on the $M_{n,theo}$= 10000. Meanwhile, it

should be noted that unreacted PEG, P*t*BA and PMMA precursors were easily removed from the reaction mixture by dissolution-precipitation.

^{1}H NMR analysis of poly(oxanorbornene)-*g*-PMMA-P*t*BA-PEG indicated that the polymers are readily incorporated into the poly(oxanorbornenyl anthracene) by appearance of the characteristic peaks of segments and as well as disappearance of anthracene peaks as seen in Figure 4.5.

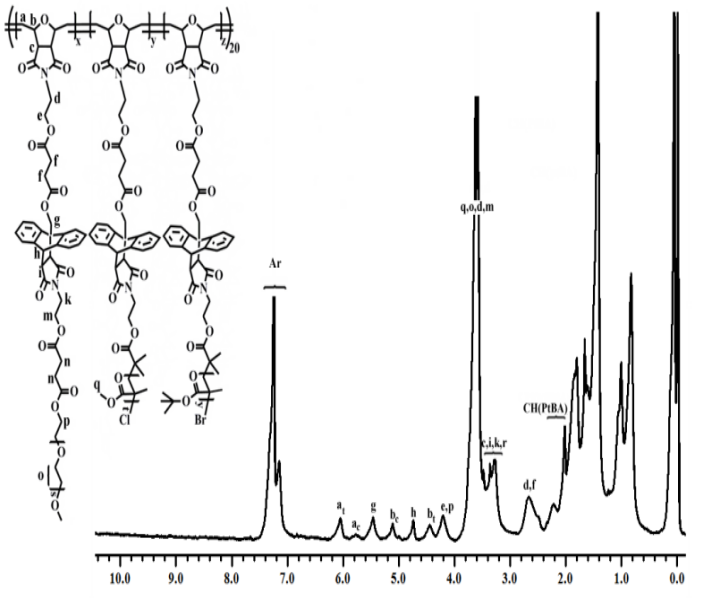


Figure 4.7: 1H NMR spectrum of poly(ONB)-g-PEG-PtBA-PMMA in CDCl3

Additionally, a GPC trace of poly(oxanorbornene)-*g*- PMMA-P*t*BA-PEG showed a shift to the higher retention time region as compared to that of poly(oxanorbornenyl anthracene). This may be due to adsorption of the graft copolymer to the stationary phase rather than selective permeation as seen in Figure 4.6.

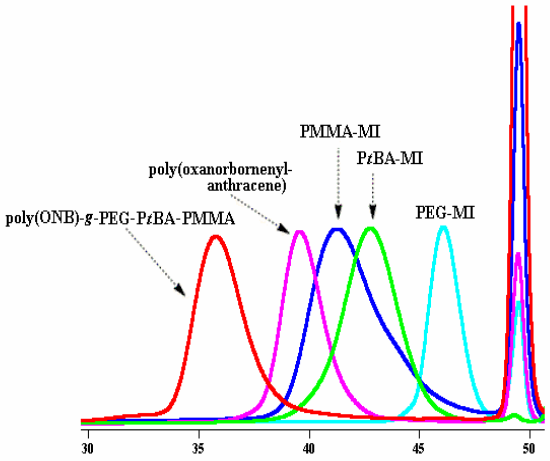


Figure 4.8: Evolution of GPC traces : PMMA-MI, P*t*BA-MI, PEG-MI, poly(oxanorbornenyl anthracene), poly(ONB)-*g*-PMMA-P*t*BA-PEG obtained from RI detection of conventional GPC at 30°C in THF.

Moreover, because of an experimental d*n*/d*c* of this graft copolymer could not be obtained correctly, TD-GPC measurement was performed by introducing a d*n*/d*c* = 0.086 mL/g derived from Diels-Alder efficiency into the instrument and subsequent the $M_{w,TDGPC}$ value was calculated as 66250 (Table 4.2).

Diels-Alder reaction efficiency was also monitored by UV spectroscopy after the decrease in absorbance of anthracene between 300 and 400 nm in the reaction medium as seen in Figures 4.14. Diels–Alder efficiency was calculated by following anthracene Conv. % = (1 – A*t* /Ao), where Ao and A*t* are initial and final absorbance values of anthracene Diels-Alder click reaction efficiencies were calculated by monitoring the disappearance of the signals corresponding to the anthracene group and found to be 97 %.

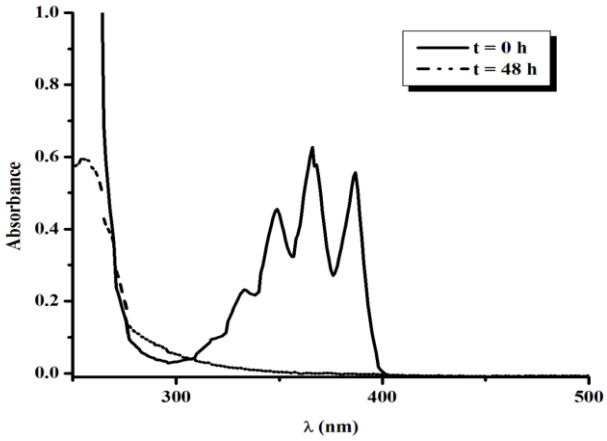
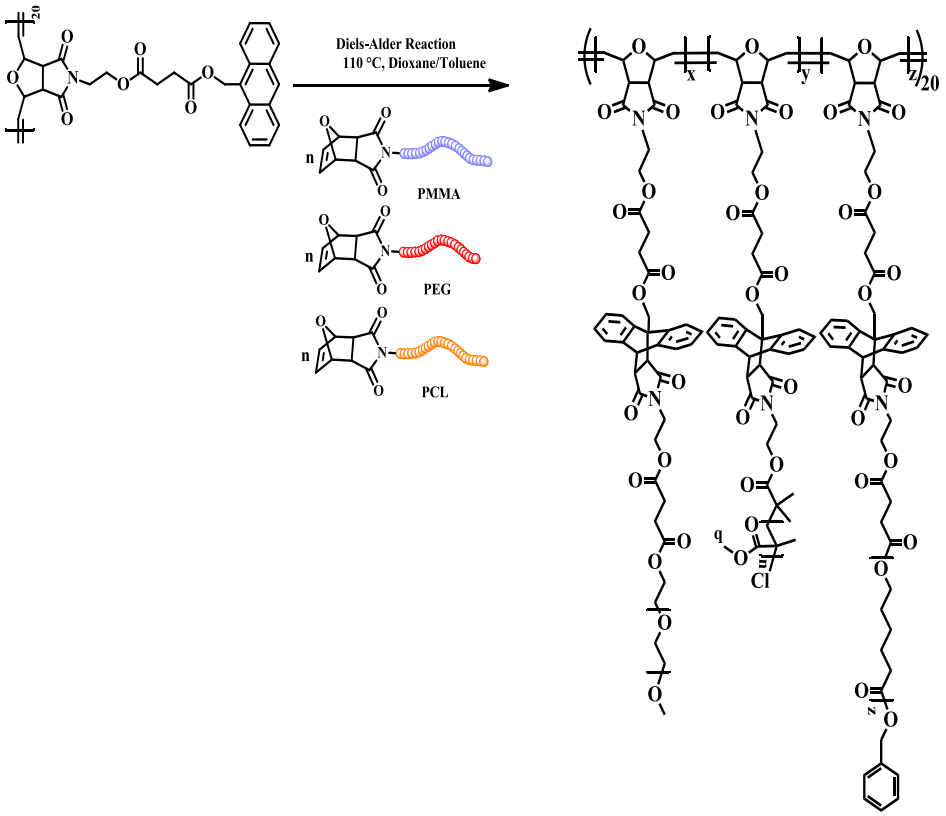


Figure 4.9: UV spectra to monitor the efficiency of Diels-Alder reaction of Poly(ONB)-*g*-PMMA-g-P*t*BA-*g*-PEG after 0 h and 48 h in CH_2Cl_2.

In a similar way, same eqivalent (8 eq) of PMMA-MI, PCL-MI, PEG-MI were grafted to poly(oxanorbornenyl-anthracene) to yield poly(ONB)-*g*-PMMA-PCL-PEG



(4.15)

7.4 equiv of PMMA, 7 equiv of PEG and 5.6 equiv of PCL per anthracene unit were employed in Diels-Alder reaction, based on the $M_{n,theo}$= 10000. Meanwhile, it should be noted that unreacted PEG, PCL and PMMA precursors were easily removed from

the reaction mixture by dissolution-precipitation.

^{1}H NMR analysis of poly(oxanorbornene)-*g*-PMMA-PCL-PEG indicated that the polymers are readily incorporated into the poly(oxanorbornenyl anthracene) by appearance of the characteristic peaks of segments and as well as disappearance of anthracene peak as seen in Figure 4.7

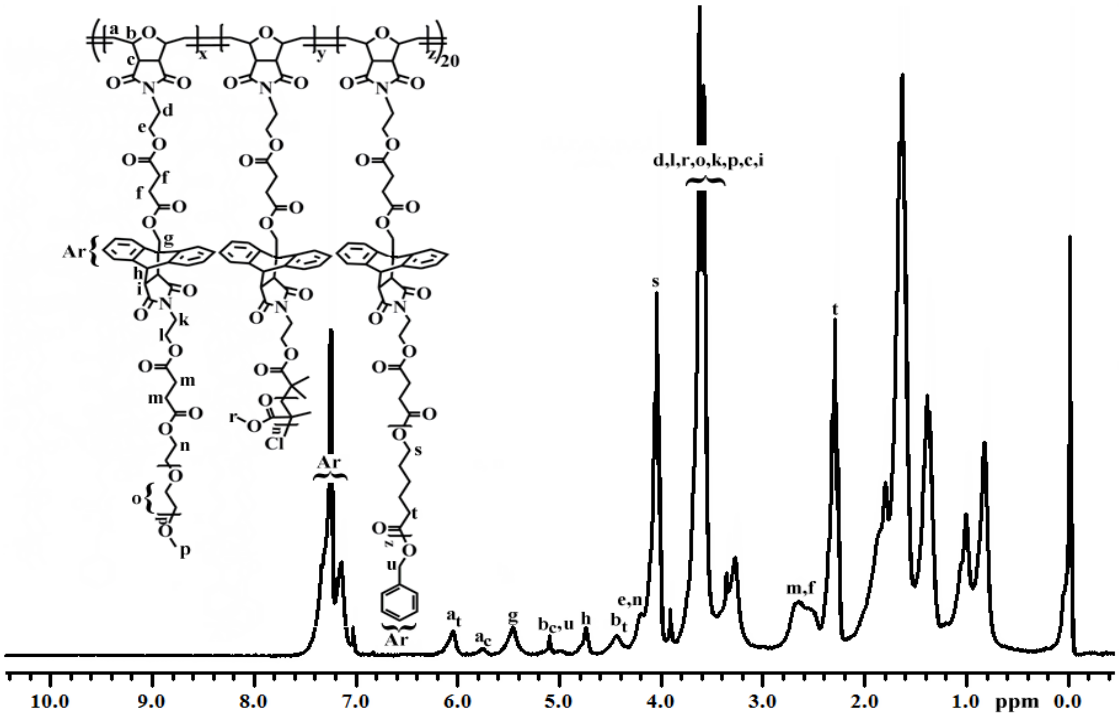


Figure 4.10: ^{1}H NMR spectrum of poly(ONB)-*g*-PEG-PCL-PMMA in $CDCl_3$

In the GPC trace of poly(oxanorbornene)-*g*-PMMA-PCL-PEG, a clear shift to higher molecular weights was observed as compared to that of poly(oxanorbornenyl anthracene), thus proving a successful grafting as seen in Figure 4.8.

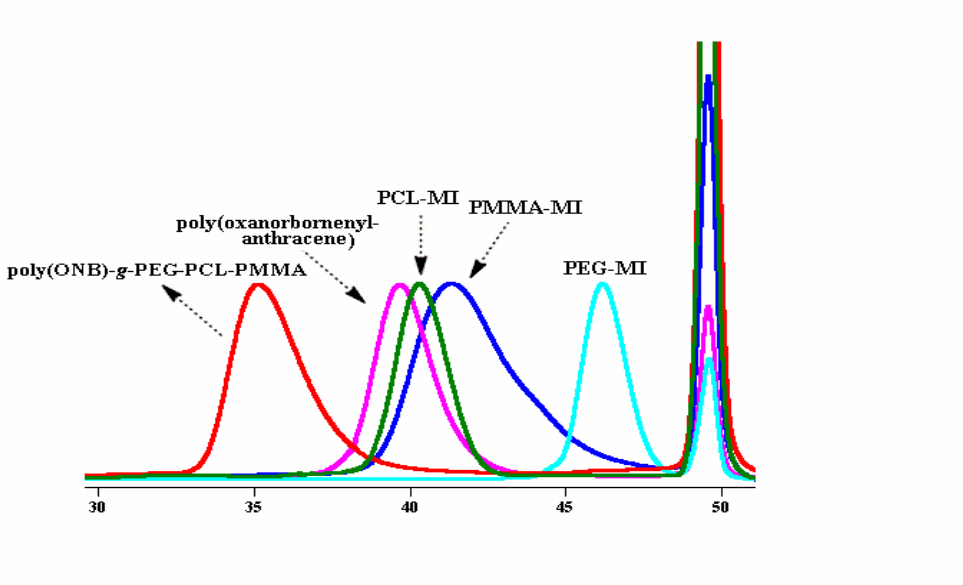


Figure 4.11: Evolution of GPC traces : PMMA-MI, PCL-MI, PEG-MI, poly(oxanorbornenyl anthracene), poly(ONB)-*g*-PMMA-PCL-PEG obtained from RI detection of conventional GPC at 30°C in THF.

The d*n*/d*c* value, 0.090 mL/g, for poly(ONB)-*g*-PEG-PCL-PMMA obtained by experimentally was introduced to the instrument so as to give $M_{w,TDGPC}$ = 58500. The experimental determination depends on a slope of RI area-polymer concentrations linear plot assuming that truly size exclusion mechanism was operative through the columns of TD-GPC (Table 4.2).

	GPC[a]			**TD-GPC**[b]		
Polymer	$M_{n,GPC}$ (g/mol)	M_w/M_n	$M_{n,theo}$ (g/mol)	M_n (g/mol)	M_w/M_n	d*n*/d*c*[e] (mL/g)
1	16000	1.16	60500[c]	66250	1.22	0.086
2	18500	1.17	51000[d]	58500	1.15	0.090

Table 4.2: The characterization of graft copolymers and their precursor

[a] Calculated from conventional GPC using linear PS standards in THF at 30 ^{0}C.

[b] Calculated from TD-GPC in THF at 35 ^{0}C .

[c] $M_{n,theo}$ = 20X(PMMA% x $M_{n,NMR}$ = 3250 of PMMA + PEG% x $M_{n,theo}$ = 840 of PEG + P*t*BA% x $M_{n,NMR}$ = 3700 of P*t*BA) + 10000

[d] $M_{n,theo}$ = 20X(PMMA% x $M_{n,NMR}$ = 3250 of PMMA + PEG% x $M_{n,theo}$ = 840 of PEG + PCL% x $M_{n,theo}$ = 2450 of PCL) + 10000

[e] Determined from a slope of RI area-concentration linear plot containing at least four different polymer concentrations assuming that truly size-exclusion mechanism was operative through the columns of TD-GPC.

5. CONCLUSIONS

As a conclusion, we here described that graft copolymers were first time successfully prepared via grafting three different maleimide end-functionalized polymers onto a main backbone in a one-pot fashion . The innovation is grafting maleimide end-functionalized polymers in one step, instead of grafting them sequantially. ROMP and Diels Alder reaction were combined to obtain graft copolymers . ATRP, ROP and esterification reactions were used for the synthesis of linear polymers . Herein the ROMP generated PONB polymer was used as a versatile main backbone for tailoring of the main chain. Grafting efficiency for all polymeric samples was monitored by using UV-Vis spectroscopy and found to be over the range of 97-99%. GPC traces of graft copolymers showed a clear shift when compared to their linear precursors, proving that graft reactions were carried out. The structures of the model graft copolymers were confirmed exactly by ^{1}H NMR, GPC and TD-GPC analyses . However, poly(oxanorbornene)-g-PMMA-g-P*t*BA-g-PEG sample displayed a different equivalence distribution of grafted polymers than poly(oxanorbornene)-g-PMMA-g-PCL-g-PEG sample. Grafted P*t*BA ratio was always lower than grafted PCL ratio. This may be attributed to the relatively branched structure of P*t*BA polymer according to PCL. The graft polymers were prepared successfully and polydispersities are 1.16 and 1.17. It should be noted that $M_{n,theo}$ values are of between $M_{w,TDGPC}$ and $M_{n,TDGPC}$.

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